
UNIVERSITY OF BIRMINGHAM

# FACTORS INFLUENCING HUMAN EXPOSURE ASSESSMENTS OF LEGACY AND "NOVEL" BROMINATED FLAME RETARDANTS VIA INDOOR DUST INGESTION

**by**

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***M.Sc, B.Sc (Hons)***

A thesis submitted to the University of Birmingham for the degree of:

**DOCTOR OF PHILOSOPHY (Ph.D)**

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**July 2016**

# ABSTRACT

Polybrominated diphenyl ethers (PBDEs) and "novel" brominated flame retardants (NBFRs) are industrial chemicals widely used in consumer products to enhance their ignition resistance. The toxicity of some BFRs has led to concern about human exposure. Ingestion of indoor settled dust appears to represent a major pathway of exposure to BFRs. The purpose of this study is to investigate the most important factors influencing human exposure assessments via dust ingestion. A new clean-up method was optimised to determine PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209) and NBFRs (PBEB, EH-TBB, BEH-TEBP, BTBPE and DBDPE) in a single sample extract via GC/ECNI-MS and GC/EI-MS. Substantial within-room and within-home spatial variability in BFR concentrations was apparent between two floor areas and between elevated surface and floor dust, due to the varying distances of sampled surfaces from potential BFR sources. With exception of DBDPE, BFR concentrations in UK elevated surface dust exceeded significantly ($p < 0.05$) those in floor dust from the same rooms. Considerable within-room and within-home temporal variability in BFR concentrations was apparent over a nine month sampling period, that is likely attributable to changes in room contents. The relative standard deviation of BFR concentrations observed in such temporal variation sample series ranged between 4% and 159%, thereby exceeding those obtained from replicate analysis of SRM2585. In view of the observed spatial and temporal variability, exposure estimates based on analysis of a dust sample taken from one specific floor area at one specific point in time may not be entirely representative of human exposure in that room. Noticeable seasonal variability in BFR concentrations was also observed between colder and warmer seasons. In 13 out of 17 floor areas, concentrations of $\Sigma_8$tri-deca-BDEs were higher in colder seasons, while those of $\Sigma_5$NBFRs were higher in warmer seasons. While concentrations of BDE-209, BTBPE, EH-TBB, and DBDPE did not differ significantly between different dust particle size fractions, those of lower brominated compounds (tri-hepta-BDEs) and BEH-TEBP were significantly higher in the finest particle size, underlining the importance of selecting the most appropriate dust particle size for the purpose of exposure assessment. BFR concentrations in researcher-collected dust (RCD) were higher than those in household vacuum dust (HHVD), and significantly higher for BDE-99, BDE-153, $\Sigma_6$tri-hexa-BDEs and – to some extent - BEH-TEBP. BFR exposure assessments using HHVD appear underestimated for lower brominated

compounds and BEH-TEBP. However, HHVD could be a viable alternative to RCD for higher brominated BFRs such as BDE-209. Significant negative correlation was observed in three rooms between concentrations of BDE-99, $\Sigma_6$tri-hepta-BDEs and BEH-TEBP and dust loading ($g/m^2$), suggesting "dilution" occurs at higher dust loadings, and that the source of these compounds and indoor dust are independent. Average concentrations of $\Sigma_6$tri-hexa-BDEs (42.7 and 26.9 ng/g), BDE-209 (1160 and 762 ng/g), BEH-TEBP (125 and 99.5 ng/g) and DPDPE (173 and 129 ng/g) in elevated surface and floor dust collected from 18 homes in Basrah, Iraq are at the lower end of those reported elsewhere. Our estimates of exposure to these contaminants via dust ingestion for the Iraqi population fall below the relevant health-based limit values.

## *Dedication*

*This thesis is dedicated to the memory of my brother*

***Ahmed***

# ACKNOWLEDGMENTS

*First and foremost, I would like to thank Allah for giving me the health and strength to pursue my dreams.*

*I am forever grateful to my supervisor* ***Professor Stuart Harrad*** *for all his guidance, assistance, encouragement, continuous support, supervision and valuable advice throughout this project. I have been extremely lucky to work with him, and I am pleased to be a part of POPs research group.*

*I acknowledge gratefully the Iraqi government for my PhD scholarship, the Iraqi Establishment of Martyrs for financial support and the Ministry of Higher Education and Scientific Research (MOHESR) for administrative support.*

*I would like to thank all the dust donors from Birmingham, UK and from Basrah, Iraq. Many thanks to our laboratory managers, Mrs. Eimear Orgill and Dr. Maria Thompson for their assistance during the work in Public Health Building and Earth Sciences labs. I would also like to thank Dr. Mohamed Abdallah, Dr. Yuning Ma and Dr. Salim Alam for their time to answer my many questions. Special thanks go to Dr. Temilola Oluseyi for all support and for her abiding friendship. I would like to thank soon to be Dr. Salim Sakaroun for continued help. Many thanks to my fellow PhD students and friends in Room 209 and 216 for all their help and happy times we have had together.*

*I would like to thank my big family and all my friends in Iraq for their encouragement and my husband Kamil for his understanding, without their support and love this work would not have been completed. Very special thanks for my daughter Marwa and my son Mostafa whom I left in Iraq, for their patience during my absence, and for my daughter Safa and my son Ali who supported me here in the UK.*

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# ABBREVIATIONS

| | |
|---|---|
| ABS | Acrylonitrile Butadiene-Styrene |
| AC | Acetone |
| ANOVA | Analysis of variance |
| ASE | Accelerated Solvent Extraction |
| ATSDR | Agency for Toxic Substances and Disease Registry |
| BFRs | Brominated flame retardants |
| Br | Bromine |
| BSEF | Bromine Science and Environmental Forum |
| Bw | Body weight |
| DCM | Dichloromethane |
| DDT | Dichloro-diphenyl-trichloroethane |
| Dwt | Dry weight |
| EA | Ethyl acetate |
| EBFRIP | European Brominated Flame Retardant Industry Pane |
| ECNI | Electron capture negative ionisation |
| EDIs | Estimated daily intakes |
| EEE | Electrical and electronic equipment |
| EFSA | European Food Safety Authority |
| EHHI | Environment & Human Health, INC |
| EI | Electron ionisation |
| EU | European Union |
| E-waste | Electronic waste |
| FIRESEAT | Fire Safety Engineering Applied To... |
| GC | Gas chromatography |
| GC-MS | Gas chromatography-mass spectrometry |
| GPC | Gel permeation chromatography |
| HIPS | High impact polystyrene |
| HPLC | High pressure liquid chromatography |
| HVS3 | High Volume Small Surface Sampler |
| IC | Inorganic carbon |
| IDL | Instrumental detection limit |
| IS | Internal standard |
| IUPAC | International Union of Pure and Applied Chemistry |
| $K_{OA}$ | Octanol-air partition coefficient |
| $K_{OC}$ | Organic carbon water partitioning coefficient |
| $K_{OW}$ | Octanol–water partition coefficients |
| LC | Liquid chromatography |
| LOD | Limit of detection |
| LOQ | The limit of quantification |

| | |
|---|---|
| LPV | Low production volume |
| M/Z | Mass to charge ratio |
| MAE | Microwave-assisted extraction |
| MID | Multiple ion detection modes |
| MRL | Method reporting limit |
| MRV | Minimum Reported Value |
| MS | Mass spectrometry |
| MW | Molecular Weight |
| NFPA | National Fire Protection Association |
| NICNAS | National Industrial Chemicals Notification and Assessment Scheme |
| NIST | National Institute of Standards and Technology |
| PAHs | Polycyclic aromatic hydrocarbons |
| PBDEs | Polybrominated diphenyl ethers |
| PCBs | Polychlorinated biphenyls |
| PINFA | Phosphorus, Inorganic and Nitrogen Flame Retardants Association |
| PM | Particulate matter |
| POPs | Persistent organic pollutants |
| PTV | Programmable temperature vaporiser |
| PUR | Polyurethane |
| PVC | Polyvinyl Chloride |
| QA/QC | Quality assurance/ quality control |
| RDS | Recovery determination standard |
| RfD | Reference dose |
| RRF | Relative response factor |
| RRT | Relative retention time |
| RSD | Relative standard deviations |
| SD | Standard deviation |
| SIM | Selected ion monitoring |
| SPE | Solid phase extraction |
| SRM | Standard reference material |
| SVOCs | Semi-volatile organic compounds |
| T3 | Triiodothyronine |
| T4 | Thyroxine |
| TC | Total carbon |
| TOC | Total organic carbon |
| TRW | Technical Review Workgroup for Metals and Asbestos |
| TV | Television |
| UNEP | United Nations Environment Programme |
| USEPA | United States Environmental Protection Agency |
| VCCEP | Voluntary Children's Chemical Evaluation Program |
| WHO | World Health Organization |

# CHAPTER 1

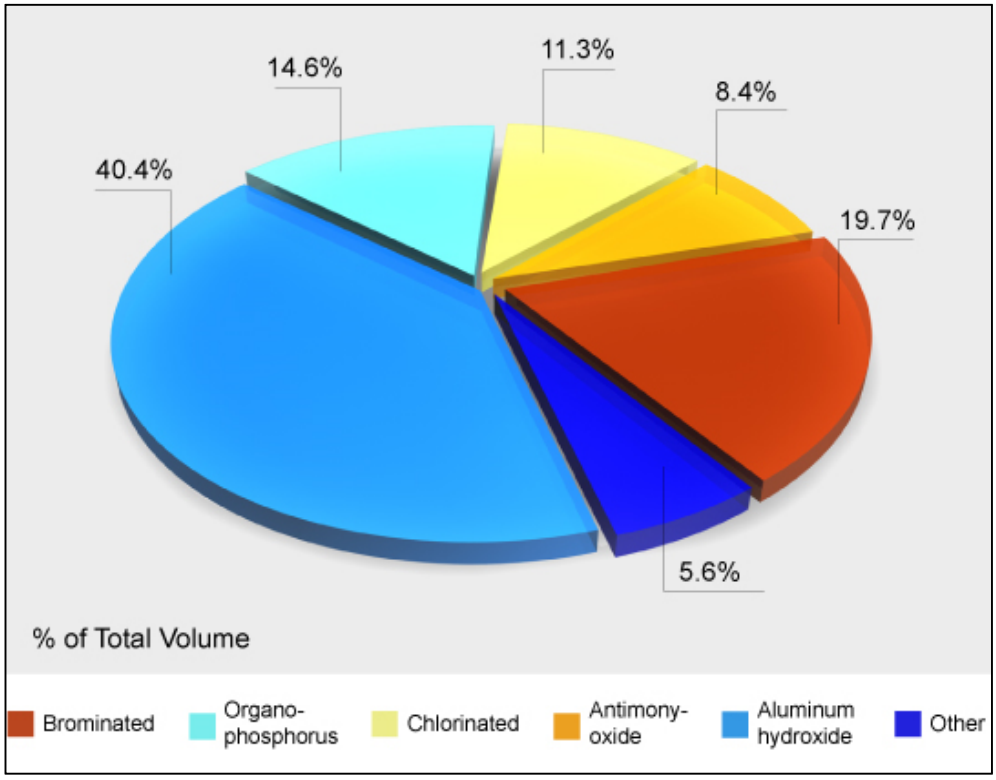
# INTRODUCTION

## 1.1 Background

Fire is one of the most serious challenges threatening human life, regardless of whether it was caused naturally or accidentally. Annually, because of fire, there are thousands of deaths and billions of dollars lost through damage to property. Nowadays, fire accidents are less common than 28 years ago. For example, in the United States, fire accidents declined by about 39 % between 1977 and 2014 (NFPA, 2015). This fact may be at least partly attributable to increased use of chemicals known as flame retardants (FRs). Flame retardants, which are applied in various materials, such as plastics, woods, paper, and textiles (Birnbaum and Staskal, 2004), "decrease the ignitability of materials and inhibit the combustion process, limiting the amount of heat released" (USEPA, 2014). The earliest flame retardant was used by the Egyptians (450 BC) and the Romans (200 BC) to reduce the flammability of wood. Over the past 60 years, advances in petroleum-based polymer science have led to production of a huge number of polymers with different properties and applications, which have enhanced demand for FRs. Today, more than 175 flame retardants exist, classified into five main families which are: (1) Inorganic flame retardants such as aluminium trioxide, magnesium hydroxide, (2) Polyphosphate, and red phosphorus, which represents about 50 % of total market volume, (3) Brominated flame retardants, (4) Chlorinated flame retardants and (5) Nitrogen-based organic flame retardants (Danish EPA, 2013). In general, FRs should contain one or more of the following elements: chlorine, bromine, aluminium, boron, nitrogen, phosphorus, or silicon in their structures, in addition to any synergist materials that are also effective (USEPA, 2014).

According to a 2012 market study, the worldwide consumption of flame retardants amounts to around 2 million tons a year, use with textiles and rubber products account for about 15 %, with the remaining 85% being used in plastics (PINFA, 2013). It was forecast that the global flame retardant market would grow at about 3.4% a year on a volume basis during the period 2013-2018. In 2013, 27% of the global FR market share was in China, followed by North America (22%) and Western Europe (22%) (IHS, 2014). Figure 1.1 shows the global consumption of flame retardants in plastics by type in 2011.

**Figure 1.1: Global consumption of flame retardants in plastics by type, in 2011 (Danish EPA, 2013)**




## 1.2 Brominated flame retardants

Brominated flame retardants (BFRs) are a group of synthetic chemicals added to a wide range of polymers, plastics, foams and textiles in furnishing, electronics and building materials to meet flame retardancy standards set by various jurisdictions worldwide, containing 50-85% bromine by weight (Danish EPA, 2016). According to the molecular structure categories, BFRs are classified into aromatic, cycloaliphatic and aliphatic compounds, implying a wide range of physicochemical properties of BFRs to match the properties of the material to be flame-retarded (DNV, 2010). Depending on their mode of incorporation into the polymers to which they are added, they are referred to as either reactive or additive BFRs. Reactive flame retardants, such as tetrabromobisphenol-A (TBBPA), are chemically bonded to the polymer. Conversely, additive BFRs, such as polybrominated diphenyl ethers (PBDEs) and hexabromocylododecane (HBCDD) are simply blended with the polymers and do not become a part of the base polymer. Additive BFRs are the most common because their application in consumer goods is less complicated than for reactive BFRs (Alaee et al., 2003). Historically, the three aforementioned BFRs are the most important types along with the polybrominated

biphenyls (PBBs). When BFRs are used additively, they are more likely to leach out of the products into the environment. An extensive body of research has reported the presence of BFRs in air, dust, soil, sediment and biota samples. Evidence of their persistence and capacity for bioaccumulation, coupled with concerns about their adverse health effects has led to widespread bans and restrictions on the manufacture and use (UNEP, 2008; 2013a; 2013b). Such bans and restrictions on the use of BFRs without relaxation of flammability standards, has likely resulted in increased production and use of alternatives referred to collectively as "novel" brominated flame retardants (NBFRs) (Covaci et al., 2011), According to the empirical data, studies suggest that some NBFRs have the same hazard profiles as "legacy" BFRs (USEPA, 2014). Global production of BFRs was estimated to be 575,000 tonne/year in 2007 and 595,000 tonne/year in 2015 (Danish EPA, 2016). As shown in Figure 1.1, brominated flame retardants are the second largest market group because of their low cost and high-performance efficiency (Birnbaum and Staskal 2004).

### 1.2.1 Mechanism of action of brominated flame retardants

Fire is a complex chemical reaction between a fuel and oxygen, involving a number of interrelated and interdependent stages. By interfering with one or more of these stages, it is possible that flame retardants will decrease the rate of material consumption. In the case of BFRs, highly reactive Br· free radicals as the material are decomposed in the fire. (USEPA, 2014). The following steps describe the action of bromine as the most effective chemical to prevent fire from developing (FIRESEAT, 2010).

For ignition to occur, number of radicals must release (reactions 1 and 2).

. $H\cdot + O_2 \rightarrow OH\cdot + O\cdot$ (1)

$\cdot O\cdot + H_2 \rightarrow OH\cdot + H\cdot$ (2)

The effectiveness of brominated flame retardants (R-Br) is to release free radical bromine

$R\text{-}Br \rightarrow R\cdot + Br\cdot$ (3)

HBr evolved from the decomposition of brominated flame retardants will interfere with the gas phase combustion process of the hydrocarbon material.

$Br\cdot + RH \rightarrow R\cdot + HBr$ (4)

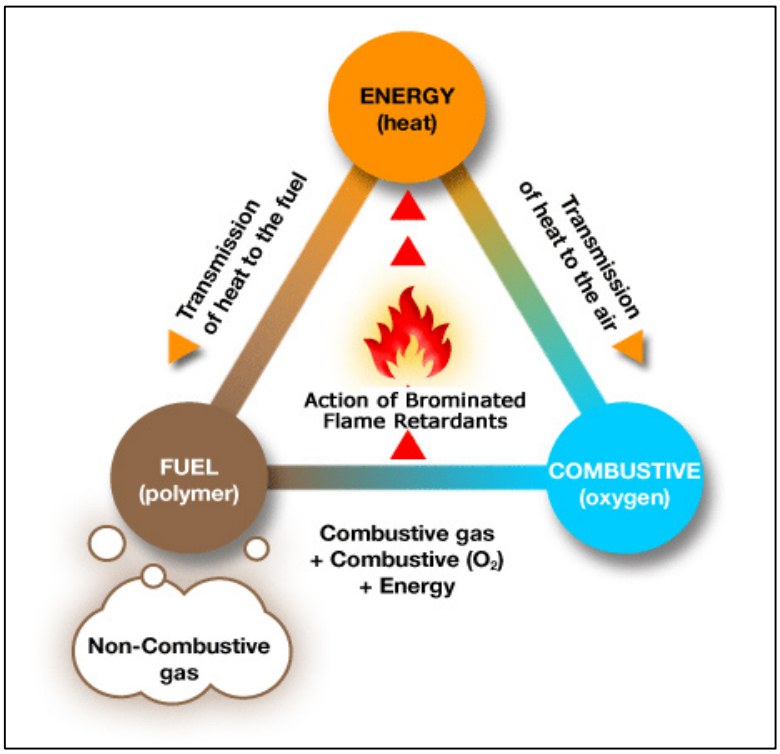
The removal of OH· and H· radicals is key to the elimination of the main chain branching step and blocking the main heat release step of hydrocarbon combustion

$HBr + H\cdot \rightarrow H_2 + Br\cdot$ (5)

$HBr + OH\cdot \rightarrow H_2O + Br\cdot$ (6)

The high-energy OH· and H· radicals formed from reactions 1 and 2 are removed by the bromine-containing flame retardant (reactions 5 and 6). Figure 1.2 presents simply the action of brominated flame retardants in the fire process.

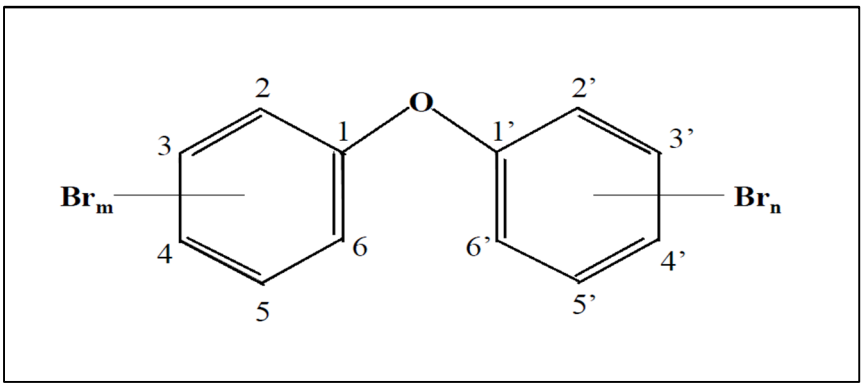
**Figure 1.2: Brominated flame retardants action to prevent fire development (EBFRIP, 2015)**




## 1.3 Polybrominated diphenyl ethers (PBDEs)

PBDEs are a family of chemicals with a common structure of a brominated diphenyl ether and have the chemical formula $C_{12}H_{(0-9)}Br_{(1-10)}O$. Any of the ten hydrogen atoms of the diphenyl ether moiety can be exchanged with bromine, resulting in 209 possible congeners. Each individual PBDE is distinguished from others by both the number of bromine atoms and the placement of those atoms (Figure 1.3). These congeners are numbered using the International Union of Pure and Applied Chemistry (IUPAC) system. (Birnbaum and Staskal 2004; Guerra et al., 2011).

**Figure 1.3: General structure of PBDEs (n+ m = 1 - 10) (USEPA, 2010)**




Since the 1970s, PBDEs have maintained an extensive presence in consumer products, such as plastics, textiles, building material, foamed furniture and electronics (WHO 1997). Commercial products of PBDEs have been marketed in three main formulations, namely: Pentabromodiphenyl ether (Penta-BDE), Octabromodiphenyl ether (Octa-BDE) and Decabromodiphenyl ether (Deca-BDE), with the trade names of DE71, DE79 and Fr-300BB for Penta-, Octa-, and Deca-BDE respectively (WHO, 1997). The commercial formulations are manufactured through the chemical reaction of bromine with diphenyl ether in the presence of an inorganic catalyst such as $AlCl_3$ (ATSDR, 2004; USEPA, 2010). The reaction conditions for PBDEs in the commercial products are not disclosed by the manufacturers, and all of the three commercial mixtures consist of mixtures of congeners with different degrees of bromination (NICNAS, 2007). However, the leading commercial Penta-BDE mixture is primarily comprised of tetra-BDEs (particularly BDE-47) and penta-BDEs (particularly BDE-99 and BDE-100), and the commercial Octa-BDE mixture comprised of hepta-BDEs and octa-BDEs. Table 1.1 lists IUPAC number and bromine substitution pattern of some selected BDEs involved in this study, along with Table 1.2 which lists the relative proportions by weight of various PBDE congeners in the commercial products.

**Table 1.1: IUPAC number and bromine substitution pattern of some BDE congeners involved in this study**

| Congener | Number of bromine atoms | Chemical name |
|---|---|---|
| BDE-28 | 3 | 2,4,4'-tribromodiphenyl ether |
| BDE-47 | 4 | 2,2',4,4'-tetrabromodiphenyl ether |
| BDE-99 | 5 | 2,2',4,4',5-pentabromodiphenyl ether |
| BDE-100 | 5 | 2,2',4,4',6-pentabromodiphenyl ether |
| BDE-153 | 6 | 2,2',4,4',5,5'-hexabromodiphenyl ether |
| BDE-154 | 6 | 2,2',4,4',5,6'-hexabromodiphenyl ether |
| BDE-183 | 7 | 2,2',3,4,4',5',6-heptabromodiphenyl ether |
| BDE-209 | 10 | 2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether |

**Table 1.2: Composition of commercial polybrominated diphenyl ethers (USEPA, 2008a; 2008b; 2010; La Guardia et al., 2006)**

| Congener | Penta-BDE | Octa-BDE | Deca-BDE |
|---|---|---|---|
| BDE-28/33 | 1% | - | - |
| BDE-47 | 28% | - | - |
| BDE-49/66 | 1% | - | - |
| BDE-99 | 43% | - | - |
| BDE-100 | 8% | - | - |
| BDE-153 | 6% | 0.15–8.7% | - |
| BDE-154 | 4% | 0.04–1.1% | - |
| BDE-183 | - | 13–42% | - |
| BDE-196 | - | 3.1–10.5% | - |
| BDE-197 | - | 11–22% | - |
| BDE-203 | - | 4.4–8.1% | - |
| BDE-206 | - | 1.4–7.7% | 2.2% |
| BDE-207 | - | 11–12% | 0.24% |
| BDE-209 | - | 1.3–50% | 97% |

### 1.3.1 Global production of PBDEs

According to the global market demand in 2001, approximately 95%, 40% and 44% of Penta-, Octa-, and Deca-BDE global production respectively was consumed in the Americas. The next highest consumption of PBDEs was reported in Asia where 2.0%, 40% and 41% of global production of Penta-, Octa-, and Deca-BDE was consumed; followed by Europe, which consumed 2.0%, 16% and 14% of global Penta-, Octa- and Deca-BDE production respectively. The rest of the world consumed 1.3%, 4.7% and 1.9 % respectively of global Penta-, Octa- and Deca-BDE production. In the Middle East, Israel and Jordan are the main producers of bromine in the world, however, no data are available for PBDEs (Guerra et al., 2011). Overall, Deca-BDE global production accounted for 83% of total PBDEs, followed by Penta-BDE (11%), and Octa-BDE (6%) (Danish EPA, 2016). While figures are not available for Penta- and Octa-BDE production in 2003, global production of Deca-BDE was 56,418 tons (Danish EPA, 2013). Table 1.3 lists total global demand for PBDE commercial products in 1994, 1999, 2001 and 2011 (Guerra et al., 2011; Danish EPA, 2013).

**Table 1.3: Total global market demand (metric tonnes) for PBDE commercial mixture of PBDEs flame retardants (Guerra et al., 2011, Danish EPA, 2013)**

| | **Global Market Demand (metric tonnes) in…** | | | |
|---|---|---|---|---|
| **PBDE Formulation** | **1994** | **1999** | **2001** | **2011** |
| Penta-BDE | 4,500 | 8,500 | 7,500 | negligible |
| Octa-BDE | 6,000 | 3,825 | 3,790 | 100-1000 |
| Deca-BDE | 30,000 | 54,800 | 56,150 | 5,000-50,000 |
| Total | 40,500 | 67,125 | 67,440 | 5,100-51,000 |

Following the phase-out of and restrictions on the production and use of PBDEs, commercial Penta-BDE has not been manufactured in Europe, Canada, Australia, the U.S.A and Japan since 2007, while there is no information on the status of its production in China. For Octa-BDE, the POP Review Committee indicates that this product was no longer produced in the EU, USA, Japan and China after 2004. However, Octa-BDE was still imported to Denmark until 2013 with polycarbonate raw materials, demonstrating that at least one country has produced this substance post-2004 (Danish EPA, 2013). Domestic production of commercial Deca-BDE in China increased from 10,000 to about 30,000 tons between 2000 and 2005 due

to the rapid growth of manufacturing activities, e.g., electronic products and automobiles (Chen et al., 2007). In the EU, Deca-BDE has been banned in electronic and electric applications since the middle of 2008 (European Court of Justice, 2008). Thus, manufacture and use of Deca-BDE has been progressively restricted and it is currently under consideration for listing under the Stockholm Convention (UNEP, 2013b). Moreover, BSEF (Bromine Science and Environmental Forum) member companies have decided to voluntarily phase out production of the Deca-BDE formulation by the end of 2013 (Hess, 2009 cited in Guerra et al., 2011). It is however, expected that PBDE formulations may maintain a – albeit reduced - presence in new electronics due to the use of recycled plastics (USEPA, 2010). Table 1.4 illustrates the market demand for PBDEs by region (Americas, Europe, Asia and the rest of the world in 2001 (Danish EPA, 2016).

**Table 1.4: Use by Region of Penta-, Octa- and Deca-BDEs (metric tonnes) in 2001 (Danish EPA, 2016)**

| PBDE Formulation | Americas | Europe | Asia | Rest of the world |
|---|---|---|---|---|
| Penta-BDE | 7,100 | 150 | 150 | 100 |
| Octa-BDE | 1,500 | 610 | 1,500 | 180 |
| Deca-BDE | 24,500 | 7,600 | 23,000 | 1,050 |
| Total | 33,100 | 8,360 | 24,650 | 1,330 |

### 1.3.2 Applications and usages of PBDEs

Prior to the end of production in 2004, Penta-BDE was used almost entirely in flexible polyurethane foam materials, such as furniture foams, mattresses, carpet padding, and car seats. Such applications constitute up to 30% of polyurethane foams. In addition, commercial Penta-BDE was used in phenolic resins, polyesters, and epoxy resins (Alaee et al., 2003).

The major uses of Octa-BDE were in acrylonitrile-butadiene-styrene (ABS) polymers at 12-18 % weight loadings in the final product. Approximately 95 % of the total Octa-BDE supplied in Europe was used in ABS. Minor uses of Octa-BDE include: polybutylene terephthalate (PBT), high impact polystyrene (HIPS), and polyamide polymers, with loadings of 12-15 % weight in the final product. (NICNAS, 2007; Danish EPA, 2013). In addition,

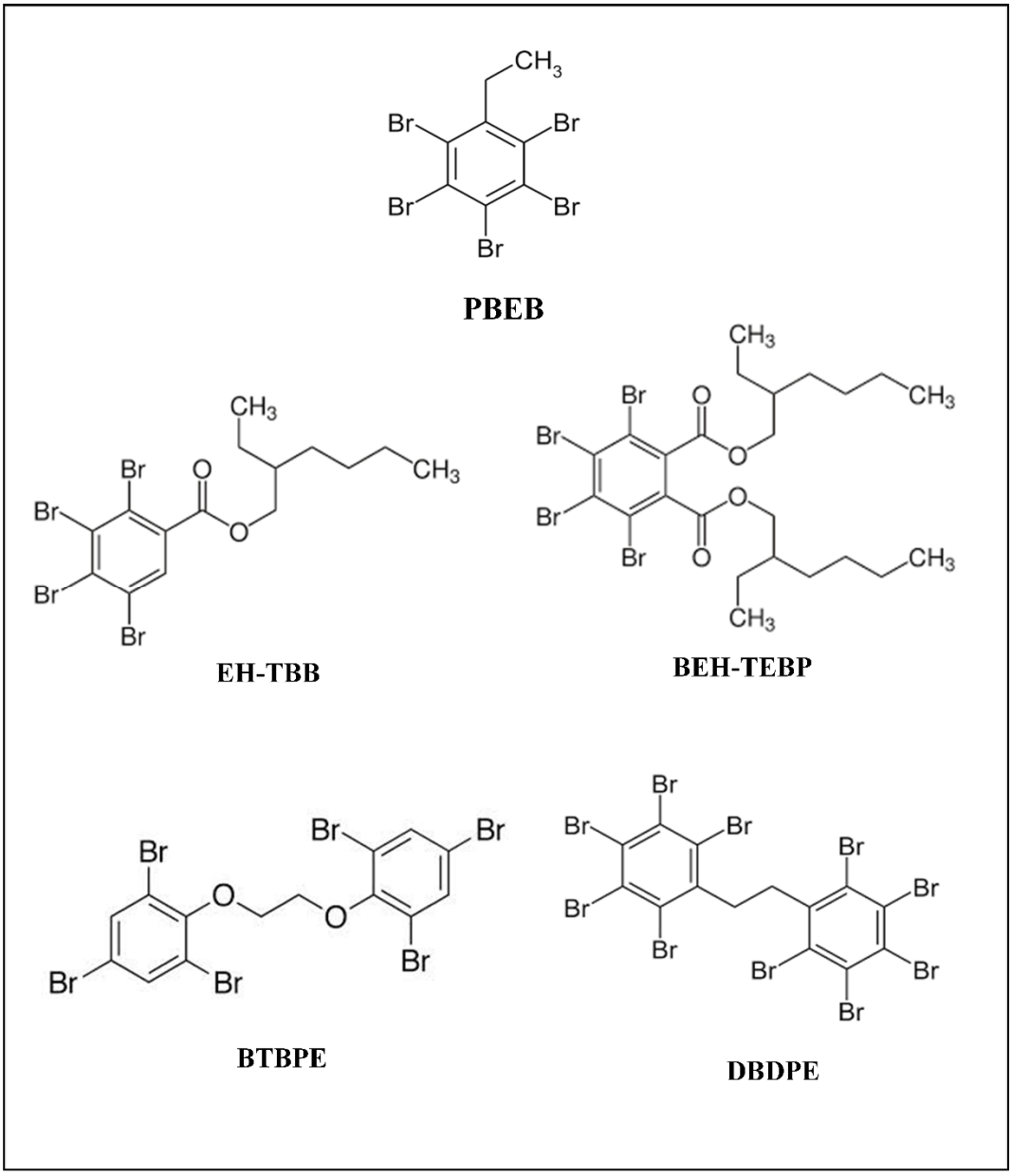
other reported uses of Octa-BDE include: nylon and low-density polyethylene, polycarbonate, phenol-formaldehyde resins and unsaturated polyesters and in adhesives and coatings. ABS containing Octa-BDE has been used for enclosures and structural parts of electrical and electronic equipment and may be present in recycled plastics and electronic waste (La Guardia et al., 2006; USEPA, 2007).

According to the USEPA (2014), Deca-BDE is used in a wide range of polymers and plastics included polyolefins, styrenics (vinyl benzene), engineering thermoplastics, thermosets, elastomers, waterborne emulsions, and coatings, which are used in diverse sectors. In the USA, the proportion of Deca-BDE use by weight is suggested to be: 26% for textiles, 26% for vehicles/transportation, 26% for building and construction materials, 13% for electrical and electronic equipment and 9% for other uses (Levchik, 2010 cited in USEPA 2014). In Europe, before the restriction in electronic applications (European Union, 2011), it was estimated that 80 % of Deca-BDE was used in television enclosures, central processing unit housing and wire and cable and 10-20 % in textiles. In addition, office equipment such as copiers, printers and fax machines, are now made using plastics that do not contain Deca-BDE (USEPA, 2014). In electrical and electronic equipment, Deca-BDE is and has been used in housings and internal components of TVs, mobile phones and fax machines, communication cables, audio and video equipment, remote controls, capacitor films, building cables, wire and cable, connectors in electrical and electronic equipment, circuit breakers, scanner components, transformer coils, as well as printing and photocopy machine components. In the textiles sector, Deca-BDE has applied to the backs of fabrics used in transportation (buses, trains, airplanes, and ships), and public spaces (theatres, hotels, conference rooms, student dormitories). In the building and construction sector, Deca-BDE has been used in film for use under the roof and to protect building areas, lamp holders, stadium seats, switches and connectors, electrical ducts and fittings, pillars for telephone and communication cables, components in analytical equipment in industrial applications, air ducts for ventilation systems and facing laminates for insulation panels (USEPA, 2014). In the transportation sector, in addition to its use in fabrics, Deca-BDE has been used in electrical and electronic equipment, reinforced plastics, as well as under hood and internal parts.

## 1.4 Novel brominated flame retardants (NBFRs)

Growing evidence suggests that PBDEs are persistent and bioaccumulative toxicants, which affect negatively the nervous system, as well as fertility, the liver and the thyroid (WHO, 2003; USEPA, 2006; 2008a; 2008b; 2008c; Noyes et al., 2010; EFSA 20012). As mentioned in section 1.2, both the Penta- and Octa-BDE commercial mixtures were banned or phased out in 2004 in the EU, the USA and many parts of the world, and are now listed under the Stockholm Convention on Persistent Organic Pollutants (POPs) (UNEP, 2008). In addition, Deca-BDE has been proposed for listing under the Stockholm Convention on (POPs) (UNEP, 2013b). Bans and restriction on the use of established BFRs have resulted in the production of alternatives such as Novel Brominated Flame Retardants (NBFRs) to comply with flammability standards. The term NBFRs refers to brominated flame retardants which “are new to the market or recently observed in the environment due to the restrictions and bans on the use of some “legacy” BFRs” (Covaci et al., 2011). Other terms, such as "alternate", “emerging", or "non-PBDEs" have also been used to refer to these BFRs (Covaci et al., 2011, Brown et al., 2014). It has been indicated that the NBFRs are urgently required because any non-halogenated substituting chemicals can involve significant costs, as industries must adapt their products for all required performances and product standards. For example, for electrical and electronic equipment (EEE), the materials with non-brominated FRs are 10-30% more expensive than materials with brominated flame retardants (Danish EPA, 2016). The most common NBFRs replacing PBDEs are: a mixture of 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) and bis (2-ethylhexyl)3,4,5,6-tetrabromophthalate (BEH-TEBP) under the trade name Firemaster 550 as replacement for Penta-BDEs; 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE) as a replacement for Octa-BDE, and Decabromodiphenylethane (DBDPE) as a replacement for Deca-BDE (de Wit et al., 2011). Figure 1.4 illustrates the chemical structure of selected NBFRs included in this study.

**Figure 1.4: Chemical structure of selected NBFRs included in this study, PBEB (Pentabromoethylbenzene), EH-TBB (2-ethylhexyl-2,3,4,5-tetrabromobenzoate), BEH-TEBP (bis (2-ethylhexyl) 3,4,5,6-tetrabromophthalate), BTBPE (1,2-Bis(2,4,6-tribromophenoxy)ethane tribromophenoxy) ethane) and DBDPE (Decabromodiphenylethane)**




### 1.4.1 Global production of Novel brominated flame retardants (NBFRs)

The exact global production volume of NBFRs is unclear, however, it was estimated to be 180,000 tonne/year in the mid-2000s, and growing by around 5% per year (Harju et al., 2009; Covaci et al., 2011). BTBPE was marketed under the trade name FF 680 and was first produced in the mid-1970s by Great Lakes Chemical Corporation, Arkansas, USA, now a part

of Chemtura (de Wit et al., 2011; EFSA, 2012). In the US, 4,500–22,500 metric tons a year was produced between 1986 and 1994. After 1998, BTBPE production declined to between 450 and 4,500 ton/year, (Hoh et al., 2005; de Wit et al., 2011). Global consumption of BTBPE was an estimated 16,710 tons in 2001 (Verreault et al., 2007, cited in de Wit et al., 2011). No information about the production volume of BTBPE in China is available, while it was listed as low production volume (LPV) in the European Union (Harju et al., 2009; EFSA, 2012).

In the mid-1980s, DBDPE was available under different trade names such as Saytex 8010 and Firemaster 2100 (USEPA, 2014). DBDPE is considered as a low production volume in Europe, produced by Albemarle (Harju et al., 2009). European production was an estimated few thousand metric tons, mainly in Germany in 2001. However, in China, DBDPE was reported as the second most heavily produced BFR after BDE-209. Chinese production was an estimated 12,000 metric tons in 2007 (Shi et al., 2009), increasing 80% annually. (Zhang et al., 2009).

Annual production of BEH-TEBP (trade name DP 45) was estimated to be 450-4,500 tons between 1990 and 2006 (USEPA, 2010; de Wit et al., 2011). The main producer in Europe is Chemtura. BEH-TEBP together with EH-TBB are the major compounds in Firemaster 550 (EH-TBB/BEH-TEBP ratio 4:1) used as a replacement for Penta-BDE (Stapleton et al., 2008; EHHI, 2013). EH-TBB was first produced by Great Lakes Chemicals more than 35 years ago. No information is available about EH-TBB production, although it is known to have been produced in the USA (Hoh et al., 2005; de Wit et al., 2011). Finally, PBEB was produced by Dead Sea Bromine Group Ltd in the 1970s and 1980s. In 2002, PBEB production was an estimated 10-1000 tons and thus classified as a LPV product (Harju et al., 2009).

### 1.4.2 Applications and usages of NBFRs

As replacements for PBDEs, NBFRs are being used in materials, polymers and resins that were treated previously with restricted BFRs. Table 1.5 summarises the range of materials treated with different NBFRs.

**Table 1.5: NBFR-treated materials (Harju et al., 2009, Covaci et al., 2011; EFSA, 2012)**

| NBFR | CAS No | Materials/polymers/resins |
|---|---|---|
| BTBPE | 37853-59-1 | Thermoplastics |
| | | Acrylonitrile butadiene styrene terpolymer (ABS) |
| | | High impact polystyrene (HIPS) |
| DBDPE | 84852-53-9 | Styrenics |
| | | Polyester and vinyl ester resins |
| | | Textiles |
| EH-TBB | 183658-27-7 | Polyurethane (PUR) foam |
| | | Polyvinyl Chloride (PVC) |
| BEH-TEBP | 26040-51-7 | Polychloroprene (Neoprene) |
| | | Polyvinyl Chloride (PVC) |
| PBEB | 85-22-3 | Unsaturated polyesters, styrene |
| | | Butadiene copolymers |
| | | Textiles |

Depending on requirements, NBFR treated materials are applied in various consumer products. ABS, HIPS, PUR, PVC, and textiles are used worldwide in a wide range of products. ABS is normally used in housings, machines, toys, dashboards, equipment for refrigerators, telephones and other consumer electronics; HIPS is used in housings of electronic products and wiring parts; PUR is used in furniture, sound insulation, padding panels, packaging, imitation wood and transportation; PVC is used in, cables, wires, floor mats, and industrial sheets, while finally, textiles are used in back coatings of and to impregnate carpets, vehicle seating, and furniture in homes, offices and public buildings and transportation (Harju et al., 2009).

## 1.5 Physicochemical properties of PBDEs and NBFRs

PBDE commercial products are solids at room temperature, not flammable and do not present a physico-chemical hazard (USEPA, 2010). They are hydrophobic contaminants (highly water insoluble) and typically have high log octanol-water partition coefficients ($K_{OW}$).Table 1.6 illustrates physicochemical properties of PBDEs involved in this study.

**Table 1.6: Physicochemical properties of selected BDEs involved in this study (Harner and Shoeib 2002; Tittlemier et al. 2002; ATSDR, 2004; USEPA, 2010)**

| BDE | Molecular weight | Water solubility mg/L (@ 25ºC) | Log $K_{OW}$ | Log $K_{OA}$ (@ 25ºC) | Log $K_{OC}$ | Vapour pressure (Pa) (@ 25ºC) |
|---|---|---|---|---|---|---|
| BDE-28 | 407.1 | 0.07 | 5.94 | 9.5 | 3.91 | $6.51\times10^{-4}$ |
| BDE-47 | 485.82 | 0.001−0.002 | 6.81 | 10.53 | 4.12 | $5.52\times10^{-5}$ |
| BDE-99 | 564.75 | 0.009 | 7.32 | 11.31 | 4.34 | $7.94\times10^{-6}$ |
| BDE-100 | 564.75 | 0.04 | 7.24 | 11.13 | n.a | $7.07\times10^{-6}$ |
| BDE-153 | 643.62 | 0.001 | 7.9 | 11.82 | n.a | $5.80\times10^{-6}$ |
| BDE-154 | 643.62 | 0.001 | 7.82 | 11.92 | n.a | $2.64\times10^{-7}$ |
| BDE-183 | 722.4 | 0.002 | 8.27 | 11.96 | n.a | n.a |
| BDE-209 | 959.17 | <0.001 | 6.3- 12.6 | 13.21 | 6.30 | $9.28\times10^{-9}$ |

Similar to PBDEs, NBFRs are highly hydrophobic compounds, displaying low volatility and high $K_{OW}$. However, differences in molecular structure between PBDEs and their NBFR replacements results in differences in physicochemical properties. For example, the ethane bridge between the aromatic rings in the DBDPE molecule makes it more flexible and hydrophobic than BDE-209, with consequences for its environmental fate and behaviour (Covaci et al., 2011). In general, BTBPE, BEH-TEBP and DBDPE possess lower vapour pressures and higher log $K_{OA}$ compared with Octa, Penta- and Deca-BDE, respectively. Table 1.7 lists the physicochemical properties of selected NBFRs.

**Table 1.7: Physicochemical properties of selected NBFRs involved in this study (Covaci et al., 2011; de Wit, 2011; FESA, 2012; de Jourdan 2012)**

| NBFR | Molecular weight | Water solubility (mg/L @ 25° C) | Log $K_{OW}$ | Log $K_{OA}$ (@ 25°C) | Log $K_{OC}$ | Vapour pressure (Pa) (@ 25°C) |
|---|---|---|---|---|---|---|
| PBEB | 500.65 | $3.50\times10^{-4}$ | 6.76 | n a | 5.04 | $3.20\times10^{-4}$ |
| EH-TBB | 549.92 | $1.10x10^{-5}$ | 7.73 | 12.34 | 5.59 | $4.57\times10^{-6}$ |
| BTBPE | 687.64 | $1.90\times10^{-5}$ | 8.31 | 15.67 | 5.89 | $3.88\times10^{-10}$ |
| BEH-TEBP | 706.14 | $1.60\times10^{-6}$ | 9.34 | 16.86 | 6.45 | $1.55\times10^{-11}$ |
| DBDPE | 971.22 | $2.10\times10^{-7}$ | 11.1 | 19.22 | 7.00 | $6.00\times10^{-15}$ |

### 1.5.1 Impact of physicochemical properties on the environmental behaviour of BFRs

Knowledge of the physicochemical properties of substances provides information about their potential environmental fate and behaviour. The most important of these physicochemical properties are molecular weight (MW), vapour pressure ($V_P$), octanol/air partitioning coefficient ($K_{OA}$), octanol/water partition coefficient ($K_{OW}$), water solubility and organic carbon/water partitioning coefficient) ($K_{OC}$) (USEPA; 2010; USEPA 2014).

#### 1.5.1.1 Molecular weight

Depending on their molecular weight, chemicals show diverse behaviour in environmental and biological systems. With specific regard to PBDEs, variations in the degree of bromination, drive variations in physicochemical properties such as vapour pressure, hydrophobicity and lipophilicity, which in turn lead to congener-specific variations in environmental fate and behaviour. For example, while those less brominated congeners prevalent in the commercial Penta- and Octa-BDE formulations are more bioaccumulative in aquatic biota; higher brominated congeners, such as BDE-209 predominated in sediments. However, potential degradation of higher brominated compounds could yield lower brominated PBDEs that display stronger bioaccumulation characteristics than BDE-209 itself (Dominguez et al., 2011).

### 1.5.1.2 Vapour pressure ($V_P$)

Vapour pressure is a useful indicator to determine the potential of chemicals to volatilise from surfaces to the atmosphere. Inhalation is less likely to be a substantial pathway of exposure to chemicals with a vapour pressure < $10^{-6}$ mm Hg ($10^{-4}$ Pa). Conversely, inhalation is likely significant for chemicals with a vapour pressure > $1\times 10^{-4}$ mm Hg ($10^{-2}$ Pa) (USEPA, 2014). Chemicals including many BFRs that possess a vapour pressure between $1 \times 10^{-8}$ and $1 \times 10^{-4}$ mm Hg partition between the gas and particulate phases and are thereby considered semi-volatile. (USEPA; 2010; USEPA 2014; USEPA 2015). The equilibrium between the two phases is controlled by the vapour pressure, the surrounding air temperature, and the concentration and chemical composition of airborne particulate matter. $V_p$ of PBDEs decrease with increasing molecular weight and degree of bromination (USEPA 2010).

### 1.5.1.3 Octanol-air partition coefficient ($K_{OA}$)

Octanol-air partition coefficient ($K_{OA}$) is a parameter that describes the partition of SVOCs between the gas phase and organic matter such as that found in airborne particles. Commonly expressed as log $K_{OA,}$ it is the ratio between the concentration of the chemical in air and its concentration in octanol at the equilibrium state (Harner and Shoeib, 2002). As with $V_p$, log $K_{OA}$ depends on the temperature. Higher log $K_{OA}$ values implies stronger binding to the organic content of particles (Wania et al., 2002; Li et al., 2006; Weschler and Nazaroff, 2010). As shown in tables 1.6 and 1.7, log $K_{OA}$ values fall between 9.5 and 13.2 for PBDEs and between 12.3 and 19.2 for our target NBFRs. This indicates that BFRs will deposit readily from the gas phase into indoor dust, soil and vegetative biomass. In addition, the wide range of log $K_{OA}$ values implies varying abundance of these pollutants in particulate phases (Su et al., 2007; USEPA 2010).

### 1.5.1.4 Water solubility and octanol/water partition coefficient ($K_{OW}$)

As shown in Tables 1.6 and 1.7, in general, PBDE water solubility values ($1 \times 10^{-3}$ - $4 \times 10^{-2}$ mg/L) are higher than those of NBFRs ($2.1\times 10^{-7}$- $3.5\times 10^{-4}$). Water solubility is strongly inversely related to the octanol/water partition coefficient ($K_{OW}$). Commonly expressed as log $K_{OW}$, this is an important property for assessing the environmental fate and behaviour of chemicals. As can be seen from the Tables 1.6 and 1.7 lower brominated FRs have lower log $K_{OW}$ values. Generally, organic chemicals with a log $K_{OW}$ value ≥ 5.0, are very hydrophobic (USEPA 2010), thereby displaying a high tendency to sorb to organic carbon in sediments,

soils, and indoor dust and – when combined with a resistance to metabolism - possess a marked capacity for bioaccumulation.

#### 1.5.1.5 Organic carbon water partitioning coefficient ($K_{OC}$)

Another important physiochemical property is the organic carbon: water partitioning coefficient ($K_{OC}$), which provides an indication of a chemical to leach from soil to groundwater, and to partition from the aqueous phase of water bodies to suspended solids and sediment. Chemicals with high $K_{OC}$ values are strongly sorbed to soil (USEPA 2010; USEPA 2014). In general, as shown in tables 1.6 and 1.7, log $K_{OC}$ values for PBDEs (3.9- 6.3) are slightly lower than by those of their replacements (log $K_{OC}$ of NBFRs 5.8-7).

## 1.6 Environmental levels of PBDEs and NBFRs

The environmental transport of POPs has been described elsewhere as "the potential movement of a chemical after it is released to the environment, within and between each of the environmental compartments, air, water, soil, and sediment" (USEPA, 2015). PBDEs and NBFRs as both semi-volatile organic compounds (SVOCs) and additive flame retardants, can be released from treated products and enter the environment via several ways. These include: volatilisation and leaching from treated products, partitioning to indoor dust, leaching from landfills and recycling of waste products (Segev et al. 2009). As a consequence of their persistence and potential for long-range atmospheric transport, PBDEs (particularly BDE-209) and NBFRs have been detected in Arctic media, transported on airborne particulates rather than the gas phase (Law and Herzke, 2011). The first detection of PBDEs was in 1979 in soil and slug samples from the USA, with the first detection in vertebrates (fish and marine mammals collected from the Baltic Sea) was in the 1980s (Andersson and Blomkvist, 1981 cited in Law and Herzke, 2011). Since the 1980s, in addition to indoor environments, BFRs have been detected in outdoor air (Newton et al., 2015) soils (Drage et al., 2016), lakes (Venier et al., 2014), sediments (Gevao et al., 2014) and the marine environment (Webster et al., 2008). By comparison with legacy BFRs, the occurrence of NBFRs in the environment is at lower levels, however, the last few years has seen a rise in contamination with NBFRs (Law and Herzke, 2011). Today, evidence is emerging that suggests levels of PBDEs and HBCDD in the environment are decreasing in response to restrictions on their use. In a comprehensive study, Harrad (2015) collated and reviewed critically UK data on environmental levels of POP-BFRs published between 1999 and March 2015. This study revealed that, despite a lack

of evidence that UK human body burdens of Penta-BDE congeners have responded to the restrictions introduced in the mid-2000s, environmental concentrations of PentaBDE congeners such as BDE-47 and BDE-99 have declined. Evidence for temporal trends regarding HBCDD, Octa-BDE and Deca-BDE is less clear cut. Interestingly, despite the high UK levels of BDE-209 in abiotic matrices such as indoor dust, the concentrations of this congener in UK human milk are amongst the lowest reported to date, suggesting that BDE-209 bioavailability from indoor dust is likely very low (Harrad, 2015). Further afield, in China, Yu et al., (2016) reviewed the available literature on BFR (PBDEs, HBCDDs, TBBP-A and NBFRs) contamination of abiotic and biotic matrices in China. The study concluded that high concentrations of PBDEs in the environment were associated with e-waste disposal processing, but presented no evidence of this for other BFRs. No clear evidence of a decreasing trend for PBDEs in China was found (Yu et al., 2016).

### 1.6.1 Levels of PBDEs and NBFRs in indoor and outdoor air

Depending on their vapour pressure and $K_{OA}$, as SVOCs BFRs can volatilise from treated products and be abundant in both gaseous and particulate phases. The partitioning between the two phases is mainly driven by atmospheric temperature. It is expected that at a given temperature, lower brominated compounds are more abundant in the gas phase, while higher brominated congeners are more prevalent in the particle phase (Weschler and Nazaroff, 2010, Harner and Shoeib, 2002). At a given room temperature, around 96-98% of BDE-28 was predicted to be in the gas phase, while 20% of BDE-47, 60-90% of penta-hepta-BDEs and almost 100% of BDE-209 were predicted to be in the particle phase (Chen et al. 2006, cited in Besis and Samara, 2012).

A review by Besis and Samara (2012) summarised the situation regarding PBDEs in indoor and outdoor air from different countries around the world. It is difficult to compare PBDEs levels in air samples between countries, due to the different number of individual congeners, sampling method (passive or active) and the atmospheric phase sampled (vapour, particle or both). PBDEs were detected in indoor air samples from the UK (Harrad et al., 2004), Germany (Fromme et al., 2009) Denmark (Vorkamp et al., 2011), Sweden (Thuresson et al., 2012), USA (Johnson-Restrepo and Kannan, 2009), Canada (Wilford et al., 2005), China (Chen et al., 2008), Japan (Takigami et al., 2009) and Australia (Toms et al., 2009b). Concentrations were variable between countries. For the above-mentioned countries, PBDE concentrations

were between 17-55 pg/$m^3$ in Japan and 210-3980 pg/$m^3$ in the USA. In Norway, Cequier et al., (2014) reported that the maximum concentration of BDE-209 in indoor air samples was 4150 pg/$m^3$ with median concentrations of 3.8 pg/m3 (n =47).

In outdoor air samples, BFRs were detected at low levels compared with those in indoors. In the UK, Harrad et al., (2004) reported that for each of BDE-47, BDE-99 and BDE-100 concentrations in indoor air were 100 times higher that outdoor. In the USA, Hoh et al., (2005) found that ΣPBDE concentrations ranged between 10 and 85 pg/$m^3$, with BDE-47 predominant. In China, Chen et al. (2006) found concentrations of Σtri-hepta-PBDEs ranged between 87.6 and 1941 pg/$m^3$ with BDE-47 and BDE-99 were predominant.

Recently, in addition toPBDEs, more attention has been paid to NBFRs. Low concentrations of NBFRs were detected in air samples. In Sweden, Newton et al., (2015) reported that BEH-TEBP and DBDPE in indoor air ranged < 35- 150 pg/$m^3$ and < 90- 250 pg/$m^3$ with detection frequencies of 15% and 8% for BEH-TEBP and DBDPE respectively. In China, in office air samples, Newton et al., (2016) found BDE-209 was predominant with an average concentration of 2700 pg/$m^3$, while both Penta- and Octa- were present only at very low concentrations. For NBFRs, the study reported that only EH-TBB and DBDPE were detected, and only at very low concentrations. In the UK, Drage et al., (2016) investigated PBDEs in outdoor air samples from 8 sites, reporting that the average concentrations of BDE-209, Σtri-hepta-BDEs, and ΣPBDEs were 150, 49, and 180 pg/$m^3$ respectively. The study revealed a negative correlation between PBDE concentrations and the distance from the city centre. For NBFRs, BEH-TEBP and DBDPE were identified in the air samples.

### 1.6.2 Levels of PBDEs and NBFRs in surface water

PBDEs and NBFRs are hydrophobic contaminants with log $K_{OW}$ values > 5.0, thus compared with sediments and soil sample, monitoring BFRs in water samples is less attractive due to the very low concentrations. (USEPA, 2010).

As a source of fresh water, lakes are important. Yang et al., (2014a) determined tri-to-hexa-BDEs concentrations in 9 English lakes between 2008 and 2012. The concentrations of Σtri-hexa-BDEs ranged from 9.2 to 171.5 pg/L with an average of 61.9 pg/ L. Spatial variation was found between lakes, however no correlation was detected between PBDE concentrations and population density. In addition, no evidence a decline in concentrations during the

sampling period (Yang et al., 2014a). Another study in the USA, from 18 stations on the five Great Lakes' water, Venier et al. (2014) reported that the average concentrations of Σtri-deca-BDEs (112 pg/L) was dominated by BDE-47 and BDE-99 with average concentrations of 26.8 and 26.4 pg/L respectively followed by BDE-209 (9.5 pg/L). Average concentrations of BEH-TEBP, EH-TBB and other NBFRs were 10.4, 5.6 and < 1.1 pg/L respectively (Venier et al., 2014).

In sea water from the European Arctic, Möller et al., (2011) reported that the concentration of $\Sigma_{10}$PBDEs (tri-deca) in dissolved water and suspended phases of seawater ranged from 0.03-0.64 pg/L, with BDE-47 and BDE-99 predominant. In the marine environment of Hong Kong, PBDE concentrations ranged between 11-62 pg/L in the dissolved phase, and between 26 to 33 pg/L in the suspended phase (Wurl et al. (2006).

### 1.6.3 Levels of PBDEs and NBFRs in sediment and soil

Sorption of chemicals to soil or sediment can be predicted by $K_{OC}$ values. Chemicals with high $K_{OC}$ value tend to sorb to soil. PBDE congener profiles in sediments are dominated by higher brominated congeners such as BDE-209. This is different from profiles in biota samples, which are dominated by lower brominated congeners, such as BDE-47 and BDE-99 (Lee and Kim 2015). Available data on the occurrence and trends of PBDEs in marine environments have been recently reviewed. In marine sediments, BFRs were detected in Canada (Grant et al., 2011), San Francisco Bay, USA (Klosterhaus et al., 2012), Gulf of Lion, France (Salvadó et al., 2012), Northern Arabian Gulf (Gevao et al., 2014), East Java Province, Indonesia (Ilyas et al., 2011), Goseong Bay, Korea (Lee et al., 2014), South China (Zhang et al., 2009) and the Scheldt estuary, the Netherlands (Verslycke et al., 2005). With the exception of the Scheldt estuary, the Netherlands (where sediment concentrations ranged 14–22 ng/g dw for tri-hepta and 240–1650 ng/g dw for BDE-209) and south China (for which sediment concentrations fell between 30–5700 ng/g dw for BDE-209); concentrations of PBDEs in other countries were very low (Lee and Kim 2015). In surficial sediments sampled along cruise transects from the Bering Sea to the central Arctic Ocean, Ma et al., (2015a) reported that $\Sigma_{24}$PBDEs (without BDE-209) in the marine sediments ranged from < MDL to 67.8 pg/g dw, with an average concentration of 9.8 ± 11.9 pg/g dw. The study pointed that the $\Sigma_{24}$PBDE concentrations show a reduction from 2008 to 2012. In another study, the same authors (Ma et al., 2015b) reported that the average concentrations of BDE-209 in surficial fjord sediments

collected down the length of Kongsfjorden, Svalbard in the Norwegian high Arctic was 79.7 ± 53.2 pg/g dw. The two Ma et al., mentioned studies reported that PBDEs did not reveal any clear spatial trend in sediment samples. Jin et al. (2008) analysed PBDEs in river sediment cores from China, finding that PBDE concentrations ranged between 1.3 - 1,800 ng/g dwt with the highest levels found at 4- 6 cm depth.

Soil represents a major sink for many organic pollutants. In Birmingham, UK, Drage et al., (2016), reported that average concentrations of BDE-209 and Σtri-hepta-BDEs in soil samples were 11 and 3.6 ng/g respectively. BFR concentrations were higher in sites closest to Birmingham city centre. In an e-waste recycling area in South China, PBDEs and NBFRs concentrations in rhizosphere soils and non-rhizosphere soils 13.9 – 351 ng/g for PBDEs and 11.6 - 70.8 ng/g for NBFRs (Wang et al., 2016) – i.e. more enriched in rhizosphere than non-rhizosphere soils. BDE-209 and DBDPE were predominant. Total organic carbon was a more pivotal controlling factor for PBDEs than for NBFRs (Wang et al., 2016). Another study (Zheng et al., 2015b) emphasised that DBDPE and BDE-209 were the predominant compounds in forest soil samples in China. Concentrations of DBDPE ranged between 25 and 18,000 pg/g, with those of BDE-209 ranging between < dl and 5,900 pg/g. In the same study, the distribution of BEH-TEBP and most PBDEs were significantly correlated with population density. In addition, the correlation between PBDEs and their replacement products indicates similar environmental behaviour (Zheng et al., 2015b). Possible debromination of BDE-209 to lower brominated congeners in soils and sediments is a major of concern (Law et al., 2014).

### 1.6.4 Levels of PBDEs and NBFRs in sewage sludge

Wastewater treatment plants may not be effective in removing PBDEs. In Hong Kong, Deng et al., (2015) reported that 52-80% and 21–45% of PBDEs remained in effluent and dewatered sludge respectively, post-sewage treatment. On the other hand, Stiborova et al., (2015) found that both lower brominated PBDEs and BDE-209 could be successfully removed from contaminated sludge under aerobic conditions. In Korea, Lee et al., (2014), studied PBDEs and NBFRs (DBDPE and BTBPE) in sludge collected from wastewater treatment plants. The study reported that concentrations of ΣPBDE in sludge ranged from 298 to 48,000 ng/g dry weight, and among 10 NBFRs, DBDPE and BTBPE were only detected in sludge samples. DBDPE and BTBPE concentrations ranged from < dl - 3100 and < dl-21.0, with average concentrations of 237 and 1.57 ng/g dwt for DBDPE and BTBPE respectively. The highest concentrations of BTBPE and DBDPE have been detected in sludge samples originated from

the industrially active areas (Lee et al., (2014). In Spain, Cristale and Lacorte (2015) evaluated the occurrence of eight PBDEs and eight NBFRs (PBEB, EH-TBB, BTBPE, BEH-TEBP and DBDPE) in wastewater from wastewater treatment plants. With the exception of BEH-TEBP, the study reported that no PBDEs or NBFRs were detected in unfiltered influent samples. However, 279 to 2299 ng/g dwt of FRs were detected in primary sludge. NBFRs represented 63–97% of the total load and BDE-209 was the most PBDE ubiquitous congener (Cristale and Lacorte 2015).

From 12 countries around the world (including the UK, Germany, USA, China and Canada) BDE-209 and DBDPE were analysed in slug samples from wastewater treatment plants (Ricklund et al. 2008). The study found that the highest levels of DBDPE were found in Germany (216 ng/g dwt) compared with Europe (81 ng/g dwt) and North America (31 ng/g dwt). The highest concentrations of Deca-BDE were found in the UK and the USA with values of 12 000 ng/g dwt and 19 000 ng/g dwt, respectively. In one of both the largest manufacturing areas for electronic products and largest dumping sites of e-wastes in China (Pearl River Delta), Peng et al., (2009) reported that PBDE concentrations in the raw wastewater ranged from 13.3 to 2496.4 ng/ L, and in sludge between 8.5- 96.2 ng/g for tri-hepta BDEs, while those of Deca-BDE in raw wastewater were between 150- 22,894 ng/ L. Kim et al. (2013), analysed PBDEs in waste biological sludge and treated biosolids from wastewater treatment plants in Canada. The study found BDE-209, BDE-99 and BDE-47 to be the predominant compounds with concentrations of 230–82,000 ng/g, 530–8800 ng/g and 420–6000 ng/g, for BDE-209, -99, and -47 respectively.

### 1.6.5 Levels of PBDEs and NBFRs in biota and food

Bioaccumulation has been defined as “the process in which a chemical substance is absorbed in an organism by all routes of exposure as occurs in the natural environment (e.g., dietary and ambient environment sources” (USEPA, 2015). Several studies have investigated PBDEs and NBFRs in various animal species and foods. Sagerup et al., (2010) investigated NBFRs levels in seven animal species from the Arctic; specifically one fish species, three seabirds, and three mammalian species. BTBPE and DBDPE were not detected in any of these species, while EH-TBB was found in all species and BEH-TEBP in only five. Concentrations of EH-TBB ranged between 378- 3460 pg/g wet wt, while those of BEH-TEBP ranged from 573-1799. Another study (Eulaers et al., (2014a) investigated muscle, liver, adipose, preen gland

and feathers in Barn Owls, and found that PBDE concentrations in tissues (7.46-903 ng/ g lw) in 2008- 2009 were lower than in those collected in 2003- 2004 (46-11,000 ng/ g lw). The authors tentatively ascribed the decline to the 2004 European ban of Penta- and Octa-BDE mixtures. By comparison (Eulaers et al, 2014a) found NBFRs to be poorly bioaccumulated (2.3%). Another study by Eulaers et al., (2014b), investigated PBDE and non-PBDE concentrations in White-tailed Eagle feathers and plasma. Concentrations were 0.03- 2.3 ng/g for PBDEs and 0.03- 1.5 ng/g for non-PBDE BFRs. The study revealed no significant correlation between the concentrations in feathers and plasma (Eulaers et al., 2014b).

PBDEs and NBFRs have been detected in human food, animal feed and baby food. In the UK, Fernandes et al., (2016) measured PBDEs in a survey of the most commonly consumed human foodstuffs and animal feed samples, Concentrations of $\Sigma_{17}$PBDEs in food samples ranged between 0.02 ng/g and 8.91 ng/g whole weight, and in animal feed samples ranged between 0.11 ng/g and 9.63 ng/g whole weight. The highest PBDE concentrations were detected in fish, processed foods and fish feeds. In home produced eggs from e-waste sites in China, PBDEs and NBFRs were detected by Zheng et al., (2016). EH-TBB and BEH-TEBP were found in low concentrations in 50% of chicken egg samples, ranged between < dl-1.82 ng/g and 1.17-2.6 ng/g for EH-TBB and BEH-TEBP respectively. In the three categories of baby food (formula, cereal, and puree) from USA and Chinese stores, Liu et al., (2014) found median concentrations of ΣPBDEs (sum of BDE-17, -28, -47, -49, -99, -100, -153, -183, and -209) were 21 and 36 pg/g for American and Chinese baby foods, respectively.

### 1.6.6 Levels of PBDE and NBFR in human tissues

PBDEs and NBFRs have been found in human milk, serum, hair and nail samples. Zhou et al., (2014), studied EH-TBB, BEH-TEBP, BTBPE, DBDPE, BDE-209 and BDE-153 in paired human serum (n=102) and breast milk (n=105) samples from Canada. Only EH-TBB and BDE-153 had detection frequencies higher than 55% in both serum and human milk samples, while detection frequencies for other BFRs were 16.7% and 32.4% for BEH-TEBP, 3.9% and 0.0% for BTBPE, 2.0% and 0.0% for BDE-209, and 5.9% and 8.6% for DBDPE in serum and milk samples respectively. Concentrations in serum and human milk were 1.6 and 0.41 ng/g lw for EH-TBB, and 1.5 and 4.4 ng/g lw a for BDE-153 respectively (Zhou et al., 2014). Abdallah and Harrad (2014) investigated PBDEs in 35 human milk samples, finding none of the hepta–nona BDEs was above the limit of quantification. The average

concentrations of Σtri-hexa-BDE and BDE-209 were 5.95 and 0.31 ng/g lw respectively. The study found that the concentration of BDE congeners were BDE-47 > BDE-153 > BDE-99. Kang et al., (2011) detected BDE-47, -99, -100, and -183 in most human hair samples from Hong Kong. BDE-47 predominated ranging between 0.86-5.24 ng/g. Another study (Tang et al., 2013) found concentrations of PBDEs in human hair samples ranged between 4.04 and 99 ng/g, with higher concentrations in females than males. In a recent study, Liu et al. (2015) investigated PBDEs and NBFRs in human hair and nails. They found that BDE-47 and BDE-99 predominated in both hair and nail samples with concentrations ranged from 11-650 ng/g and 4.6-780 ng/g in hair samples and 7.3-43 ng/g and 2.1-11 ng/g in nail samples for BDE-47 and BDE-99 respectively. For NBFRs, EH-TBB and BEH-TEBP were detected in all hair and nail samples at concentrations between 20- 240 and 11- 350 ng/g in hair samples and < 17-80 ng/g and < 9-71 ng/g in nail samples for EH-TBB and BEH-TEBP respectively (Liu et al., 2015).

### 1.6.7 Levels of PBDE and NBFR in indoor dust

A large number of investigations around the world have reported high concentrations of BFRs in indoor dust. In a comprehensive review, Besis and Samara (2012) summarised PBDE concentrations in house dust from around the world. The highest levels were reported in US dust samples with median concentrations of ΣPBDEs ranging between 1,910 and 21,000 ng/g (Johnson-Restrepo and Kannan, 2009; Batterman et al., 2009). The UK displayed the second highest PBDEs indoor levels with concentrations ranging between 2,900 and 10,000 ng/g (Harrad et al., 2008a; Sjödin et al., 2008a). For other parts of the world, around the same date, ΣPBDE median concentrations were: 950 ng/g in Canada (Harrad et al., 2009), 386 ng/g in Germany (Fromme et al., 2009), 310 ng/g in Portugal (Cunha et al., 2010), 510 ng/g in Sweden (Thuresson et al., 2012), 1941 ng/g in China (Kang et al., 2011), 700 ng/g in Japan (Suzuki et al., 2006) and 1200 ng/g in Australia (Sjödin et al., 2008a).

In the Middle East, very few studies have investigated PBDEs in indoor dust. The first study in Kuwait in 2006 reported a median concentration of ΣPBDEs of 90.6 ng/g (Gevao et al., 2006). These levels increased in 2011 to a median concentration of 356 ng/g (Ali et al., 2013). In Egypt, Hassan and Shoeib, 2015 reported that concentrations of ΣPBDEs (median = 46 ng/g) were lower than those reported in Kuwait. In Turkey, the concentrations of $\Sigma_{14}$PBDEs ranged between 29 ng/g and 4790, with a median concentration of 316 ng/g (Civan et al.,

2016). In general, concentrations of PBDEs in North America, UK and China are orders of magnitude higher than those in the Middle East. Similar to the distribution of PBDE congeners in indoor dust from the UK and China, BDE-209 was the major BFR detected in indoor dust from the Middle East.

The PBDE congener distribution pattern varied between different countries. In the USA, BDE-47, BDE-99 and BDE-209 accounted for 17%, 29% and 33% of ΣPBDEs respectively, implying that Penta-BDE was a major contributor. A similar distribution pattern was found in Canada, with ratios of 21%, 36%, and 48% for Penta-, Octa-, and Deca-BDE of ΣPBDEs respectively (Harrad et al., 2008b). In Europe, Asia, and Australia, BDE-209 made the greatest contribution to ΣPBDEs. BDE-209 accounted for between 61% in Australia (Sjödin et al., 2008a) and around 100% in the UK (Harrad et al., 2008a) of ΣPBDEs. Since the introduction of restrictions on PBDEs, their congener profile has altered. Stapleton et al., (2012), found BDE-209, BDE-99 and BDE-47 were the largest contributors to ΣPBDEs, with average contribution ratios of 48%, 19% and 18% for BDE-209, BDE-99 and BDE-47 respectively. Dodson et al., (2012) compared concentrations of BFRs (including PBDEs and NBFRs) in house dust from California USA collected in 2006 and 2011. The study found that EH-TBB, BEH-TEBP concentrations in 2011 were about twice those detected in 2006 samples and that DBDPE concentrations were 3 times higher than 2006. In contrast, concentrations of BDE-47 and BDE-99 in 2006 were twice those in 2011, with DBE-209 concentrations 20 % higher in 2006 than 2011 (Dodson et al., 2012).

Recently, in addition to PBDEs, studies have increasingly measured NBFRs, particularly EH-TBB, BEH-TEBP, BTBPE and DBDPE as PBDE replacements. In the USA (Washington state), Schreder and La Guardia, (2014) found ΣPBDEs concentrations in house dust ranged between 311 and 19,700 ng/g, which implies a significant decline in PBDE levels compared with previous studies such as those mentioned above. In addition, the PBDE congener profiles have changed, with the relative abundance of BDE-209 increasing relative to that of Penta-BDE congeners in more recent samples. Specifically, Penta-BDE levels were about one-third those measured in previous studies in 2006 (Schreder and La Guardia, 2014). Such changes in PBDE profiles in the USA was emphasised by Stapleton et al. (2014), who found that among the eight major PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-183 and BDE-209), BDE-209 predominated with a geometric mean level of 1720 ng/g. Geometric

mean concentrations of EH-TBB and BEH-TEBP were 97.0 and 604 ng/g, respectively (Stapleton et al., 2014). Of the 11 NBFRs studied, in dust samples from USA homes, EH-TBB, BEH-TEBP, BTBPE and DBDPE represented the highest concentrations in house dust. The median concentrations were 337, 186, 22.3 and 82.8 for EH-TBB, BEH-TEBP, BTBPE and DBDPE respectively (Brown et al., 2014). Another study (La Guardia and Hale 2015) reported a similar NBFR distribution profile (i.e. EH-TBB > BEH-TEBP > DBDPE > BTBPE) in indoor dust from the USA, with average concentrations of 2580, 1850, 1230 and 140 ng/g for EH-TBB, BEH-TEBP, DBDPE and BTBPE respectively.

In Europe, NBFR concentrations and profiles differ from those in the USA. In general, the major compounds in European indoor dust are DBDPE and BEH-TEBP, with EH-TBB and BTBPE present at lower levels. In the UK (classroom dust), median concentrations were 25, 96, 9 and 98 for EH-TBB, BEH-TEBP, BTBPE and DBDPE respectively (Ali et al., 2011a). Meanwhile, in Sweden, median concentrations of Penta-BDEs (sum of BDE-28, -47, -99, -100 and -153), Octa-BDEs (sum of BDE-153, -196, -197, -203, -206, -207 and -208), BDE-209, EH-TBB, BEH-TEBP, BTBPE and DBDPE were 51, 47, 320, 2.6, 61, 6.3, and 150 ng/g respectively (Sahlstrom et al, 2015).

In China, in addition to the elevated concentrations of PBDEs, high concentrations of NBFRs were detected in house dust as well. Zheng et al., (2015a) reported that ΣPBDEs ranged between 685 and 67,500 ng/g and ΣNBFRs ranged between 1460 and 50,010 ng/g in indoor dust from e-waste sites, with BDE-209 and DBDPE the major BFRs. Qi et al., (2014) investigated NBFR (EH-TBB, BEH-TEBP, BTBPE and DBDPE) concentrations in many provinces across China. ΣNBFR concentrations ranged between 6.3-20,000 ng/g with a median concentration of 720 ng/g. DBDPE was predominant (nd- 16,000 ng/g) followed by BEH-TEBP (nd- 1,600), BTBPE (0.2- 220 ng/g) and EH-TBB (nd – 6,300 ng/g). Tables 1.8, 1.9, 1.10, 1.11 and 1.12 list concentrations (average, median, and range) of PBDEs, EH-TBB, BEH-TEBP, BTBPE and DBDPE in house dust samples from around the world, along with the sampling method, and particle size analysed. In the Middle East, median concentrations of NBFRs (EH-TBB, BEH-TEBP, BTBPE and DBDPE) were < 6.8 ng/g in Kuwait (Ali et al., 2013) and < 0.8 ng/g in Egypt (Hassan and Shoeib, 2015).

**Table 1.8: Summary of concentrations (ng/g) of PBDEs in house dust, sampling method (Researcher-collected (RC) or household vacuum (HHV)) and dust particle size analysed**

| City, Country/ Sampling Year | N | BDE | Average | Median | Range | Sampling method | Particle size | Reference |
|---|---|---|---|---|---|---|---|---|
| Toronto, Canada/ 2006 | 10 | Σtri-deca-BDEs | 1,400 | 950 | 750-3,500 | RC | <500 µm | Harrad et al., 2008b |
| Vancouver, Canada/ 2007-2008 | 116 | Σtri-deca-BDEs | 5,000 | 2,200 | 10- 61,000 | HHV | <150 µm | Shoeib et al.,2012 |
| Amarillo and Austin, USA/ 2006 | 20 | Σtri-deca-BDEs | 4,800 | 3,500 | 920-17,000 | RC | <500 µm | Harrad et al., 2008b |
| Atlanta, USA/ n.a | 10 | Σtetra-deca-BDEs | n.a | 4,200 | 520-29,000 | HHV | <2000 µm | Sjödin et al., 2008 |
| North Carolina, USA/ 2009-2010 | 74 | ΣPenta-BDE | 2,153 (GM) | n.a | 152-74,560 | RC | <500 µm | Stapleton et al., 2012 |
| | | BDE-209 | 2,574 (GM) | n.a | 441-76,130 | | | |
| Washington, USA/ 2011-2012 | 20 | Σtri-deca-BDEs | 5000 | 3,860 | 311- 19,700 | RC | n.a | Schreder and La Guardia, 2014 |
| North Carolina, USA/ n.a | 49 | BDE-47 | 374 (GM) | n.a | 28.4-21,800 | RC | <500 µm | Hoffman et al., 2015 |
| | | BDE-99 | 510 (GM) | n.a | 29.8-17,280 | | | |
| | | BDE-209 | 1280 (GM) | n.a | 103-44,900 | | | |
| Bloomington, USA/ 2013 | 20 | Σtri-deca-BDEs | 4,000 | 3,650 | 122-9,730 | RC | <500 µm | Venier et al., 2016 |
| Toronto, Canada/ 2013 | 23 | Σtri-deca-BDEs | 2,550 | 1,770 | 284-9,610 | RC | <500 µm | Venier et al., 2016 |
| Birmingham, UK/ 2006 | 28 | Σtri-deca-BDEs | 45,000 | 2,900 | 360-520,000 | RC | <500 µm | Harrad et al., 2008b |
| Newcastle upon Tyne, UK/ n.a | 10 | Σtetra-deca-BDEs | n.a | 10,000 | 950-54,000 | HHV | <2 mm | Sjödin et al., 2008 |

**Table 1.8: (continued)**

| City, Country/ Sampling Year | N | BDE | Average | Median | Range | Sampling method | Particle size | Reference |
|---|---|---|---|---|---|---|---|---|
| 6 Different cities , Germany/ n.a | 10 | Σtetra-deca-BDEs | n.a | 74 | 17-550 | HHV | <2 mm | Sjödin et al., 2008 |
| Stockholm, Sweden/ 2006 | 10 | Σtri-deca-BDEs | n.a | 330 | 72-1,400 | RC | n.a | de Wit et al., 2012 |
| Stockholm, Sweden/ 2006 | 10 | Σtri-deca-BDEs | n.a | 510 | 53-4,000 | RC | n.a | Thuresson et al., 2012 |
| Gdansk, Gdynia, Sopot, Northern Poland/ 2012 | 12 | Σtri-deca-BDEs | 264 | 232 | < LD-701) | HHV | n.a | Król et al., 2014 |
| Oslo, Norway/ 2012 | 48 | Σtri-deca-BDEs | 512 | 147 | n.a- 4,460 | RC | 1-3 mm | Cequier et al., 2014 |
| Munich, Germany/ n.a | 20 | Σtetra-hepta-BDEs | 132 | 42 | 6-1,546 | HHV | <63 μm | Fromme et al., 2014 |
| | | BDE-209 | 1,233 | 950 | 10-3,748 | | | |
| Stockholm, Sweden/ 2009-2010 | 27 | Σtri-deca-BDEs | 774 (GM) | 418 | 184-310,000 | RC | n.a. | Sahlström et al., 2015 |
| Brno, Czech Republic/ 2013 | 20 | Σtri-deca-BDEs | 241 | 163 | 18-797 | RC | <500 μm | Venier et al., 2016 |
| Lagos, Nigeria/ 2014 | 12 | BDE-47 | 13 | 8 | 2.2- 50 | RC | <500 μm | Harrad et al., 2016 |
| | | BDE-99 | 31 | 14 | 1.5-170 | | | |
| | | BDE-183 | 26 | 18 | 2.9-90 | | | |
| | | BDE-209 | 420 | 390 | 77- 940 | | | |
| Kuwait city, Kuwait / 2011 | 15 | Σtri-deca-BDEs | 1,750 | 360 | 90-19,200 | RC | <250 μm | Ali et al., 2013 |
| Cairo, Egypt/ 2013 | 17 | Σtri-deca-BDEs | 248 | 57.1 | 5.04-1,918 | HHV | 250 μm | Hassan and Shoeib, 2015 |

**Table 1.8: (continued)**

| City, Country/ Sampling Year | N | BDE | Average | Median | Range | Sampling method | Particle size | Reference |
|---|---|---|---|---|---|---|---|---|
| Shenzhen and Guangzhou, Hong Kong/ n.a | 23 | Σtri-deca-BDEs | 4,203 | 1,941 | 685-18,385 | HHV | <100 μm | Kang et al., 2011 |
| Faisalabad, Pakistan/ 2011 | 15 | Σtri-deca-BDEs | 365 | 145 | 30-2,150 | RC | <500 μm | Ali et al., 2013 |
| Trang Minh,Vietnam/ 2008 | 10 | Σtri-deca-BDEs | n.a | 450 | 140-1,900 | RC | n.a | Tue et al., 2013 |
| Heilongjiang, China/ 2010 | 14 | Σtri-deca-BDEs | 2,520 | 1,700 | 240- 9,270 | n.a | n.a | Zhu et al., 2013 |
| Guangzhou, South China/ 2008 | 46 | Σtri-deca-BDEs | 3,410 | 2,690 | 564- 9,650 | RC | <149 | Chen et al., 2011 |
| Nanjing, China/ 2011 | 216 | Σtri-deca-BDEs | 311 | 109 | 0.3-9,574 | RC | <150 μm | Wang et al., 2015 |
| 23 provinces across China/ 2010 | 78 | Σtri-deca-BDEs | 3,520 | 1,110 | 8.92-37,500 | RC (brush sampling) | n.a | Zhu et al., 2015 |
| Brisbane, Queensland, Australia/ n.a | 10 | Σtetra-deca-BDEs | n.a | 1,200 | 500-13,000 | HHV | <2 mm | Sjödin et al., 2008 |
| Brisbane, Australia/ 2007-2008 | 10 | BDE-47 | 91 | 56 | n.a | RC | <2 mm | Toms et al., 2009b |
| | | BDE-99 | 184 | 87 | | | | |
| | | BDE-183 | 102 | 2.8 | | | | |
| | | BDE-209 | 377 | 291 | | | | |
| Wellington, Christchurch New Zealand/ n.a | 33 | BDE-47 | 30.2 | 24.2 | 0.3-98.0 | RC | <500 μm | Coakley et al., 2013 |
| | | BDE-99 | 51.8 | 31.5 | 3.3- 219 | | | |
| | | BDE-183 | 12.8 | 2.7 | 0.3- 238.4 | | | |
| | | BDE-209 | 2,505 | 598 | 28.8- 27,394 | | | |

GM = geometric mean, n.a = not available

**Table 1.9: Summary of concentrations (ng/g) of EH-TBB in house dust, sampling method (Researcher-collected (RC) or household vacuum (HHV)) and dust particle size analysed**

| City, Country/ Sampling year | N | Average | Median | Range | Sampling method | Particle size | Reference |
|---|---|---|---|---|---|---|---|
| Boston, US/ 2006 | 19 | 322 (GM) | 133 | <6.6- 15,030 | RC | <500 μm | Stapleton et al., 2008 |
| Vancouver, Canada/ 2007-2008 | 116 | 510 | 120 | <0.30- 18,000 | HHV | <150 μm | Shoeib et al.,2012 |
| California, US/ 2010-2011 | 27 | 1400 (GM) | 2,687 | <0.64 - 29,007 | HHV | <150 μm | Brown et al., 2014 |
| Toronto, Canada/ 2013 | 23 | 2,410 | 966 | 121-15,300 | RC | <500 μm | Venier et al., 2016 |
| Bloomington, USA/ 2013 | 20 | 918 | 240 | <dl- 15,400 | RC | <500 μm | Venier et al., 2016 |
| Oslo, Norway/ 2012 | 48 | 16.1 | 2.54 | n.a- 245 | RC | 1−3 mm | Cequier et al., 2014 |
| Munich, Germany/ n.a | 20 | 4.2 | < 3.0 | <3.0–13.6 | HHV | <63 μm | Fromme et al., 2014 |
| Antwerp, Belgium/ 2008 | 39 | 20 | 1 | <2–436 | RC | <500 μm | Ali et al., 2011a |
| Stockholm, Sweden/ 2012 | 27 | 11 (GM) | 9.1 | < 2.5- 65 | RC | n.a. | Newton et al., 2015 |
| Stockholm, Sweden/ 2009-2010 | 27 | 6.9 (GM) | 2.6 | <0.29–280 | RC | n.a. | Sahlström et al., 2015 |
| Brno, Czech Republic/ 2013 | 20 | 17 | 7.8 | <dl- 150 | RC | <500 μm | Venier et al., 2016 |
| Cairo, Egypt/ 2013 | 17 | 28.9 | 0.81 | 0.11-369 | HHV | 250 μm | Hassan and Shoeib, 2015 |
| Kuwait city, Kuwait/ 2011 | 15 | 58 | 6.6 | 0.6 – 550 | RC | <250 μm | Ali et al., 2013 |
| Faisalabad, Pakistan/ 2011 | 15 | 0.9 | 0.4 | <0.2 – 4.8 | RC | <500 μm | Ali et al., 2013 |
| 23 provinces across China/ 2010 | 81 | 130 | 0.83 | <dl- 6,300 | RC (brush sampling) | n.a | Qi et al., 2014 |

GM = geometric mean, n.a = not available

**Table 1.10: Summary of concentrations (ng/g) of BEH-TEBP in house dust, sampling method (Researcher-collected (RC) or household vacuum (HHV)) and dust particle size analysed**

| City, Country/Sampling year | N | Average | Median | Range | Sampling method | Particle size | Reference |
|---|---|---|---|---|---|---|---|
| Boston, US/ 2006 | 19 | 234 (GM) | 142 | 3.0-10,630 | RC | <500 μm | Stapleton et al., 2008 |
| Vancouver, Canada/ 2007-2008 | 116 | 330 | 99 | 10-6,400 | HHV | <150 μm | Shoeib et al.,2012 |
| California, US/ 2010-2011 | 27 | 1,096 (GM) | 2,076 | <0.64-11,422 | HHV | <150 μm | Brown et al., 2014 |
| Toronto, Canada/ 2013 | 23 | 2,650 | 431 | 69-34,500 | RC | <500 μm | Venier et al., 2016 |
| Bloomington, USA/ 2013 | 20 | 2,540 | 624 | 112- 22,800 | RC | <500 μm | Venier et al., 2016 |
| Oslo, Norway/ 2012 | 48 | 132 | 78.5 | n.a- 809 | RC | 1−3 mm | Cequier et al., 2014 |
| Antwerp, Belgian/ 2008 | 39 | 212 | 13 | <2–6,175 | RC | <500 μm | Ali et al., 2011a |
| Munich, Germany/ n.a | 20 | 436 | 343 | 25–2,274 | HHV | <63 μm | Fromme et al., 2014 |
| Stockholm, Sweden/ 2012 | 27 | 160 (GM) | 140 | <33-1,500 | RC | n.a. | Newton et al., 2015 |
| Stockholm, Sweden/ 2009-2010 | 27 | 62 (GM) | 61 | <10–340 | RC | n.a. | Sahlström et al., 2015 |
| Brno, Czech Republic/ 2013 | 20 | 60 | 42 | <dl -373 | RC | <500 μm | Venier et al., 2016 |
| Cairo, Egypt/ 2013 | 17 | 0.19 | 0.12 | <dl-1.77 | HHV | <250 μm | Hassan and Shoeib, 2015 |
| Kuwait city, Kuwait/ 2011 | 15 | 190 | 54 | 7.2 – 1,835 | RC | <250 μm | Ali et al., 2013 |
| Faisalabad, Pakistan/ 2011 | 15 | 21 | 5.8 | 1.6 – 167 | RC | <500 μm | Ali et al., 2013 |
| 23 provinces across China/ 2010 | 81 | 120 | 29 | <dl- 1,600 | RC (brush sampling) | n.a | Qi et al., 2014 |

GM = geometric mean, n.a = not available

**Table 1.11: Summary of concentrations of BTBPE (ng/g) in house dust, sampling method (Researcher-collected (RC) or household vacuum (HHV)) and dust particle size analysed**

| City, Country/Sampling year | N | Average | Median | Range | Sampling method | Particle size | Reference |
|---|---|---|---|---|---|---|---|
| Boston, US/2006 | 19 | 48.1 (GM) | 30 | 4.7-654 | RC | <500 μm | Stapleton et al., 2008 |
| Vancouver, Canada/ 2007-2008 | 116 | 65 | 30 | 1.8- 610 | HHV | <150 μm | Shoeib et al.,2012 |
| California, US/ 2010-2011 | 27 | 31.3 (GM) | 28.4 | <0.64 -626 | HHV | <150 μm | Brown et al., 2014 |
| Toronto, Canada, 2013 | 23 | 27 | 12 | <dl -157 | RC | <500 μm | Venier et al., 2016 |
| Bloomington, USA/ 2013 | 20 | 22 | 8.5 | <dl -204 | RC | <500 μm | Venier et al., 2016 |
| Oslo, Norway/ 2012 | 48 | 8.73 | 3.76 | n.a-41.9 | RC | 1-3 mm | Cequier et al., 2014 |
| Antwerp, Belgian, 2008 | 39 | 33 | 2 | <0.5–1740 | RC | <500 μm | Ali et al., 2011a |
| Stockholm, Sweden/ 2012 | 27 | 13 (GM) | 17 | < 0.76- 150 | RC | n.a. | Newton et al., 2015 |
| Stockholm, Sweden/2009-2010 | 27 | 4.8 (GM) | 6.3 | 1.1–36 | RC | n.a. | Sahlström et al., 2015 |
| Munich, Germany/ n.a | 20 | 10 | < 10 | <10–34 | HHV | <63 μm | Fromme et al., 2014 |
| Brno, Czech Republic/ 2013 | 20 | 5.8 | 3.9 | <dl -29 | RC | <500 μm | Venier et al., 2016 |
| Cairo, Egypt/ 2013 | 17 | 0.51 | 0.24 | <dl – 2.63 | HHV | <250 μm | Hassan and Shoeib, 2015 |
| Kuwait city, Kuwait / 2011 | 15 | 53 | 6.8 | 0.9 – 535 | RC | <250 μm | Ali et al., 2013 |
| Faisalabad, Pakistan/ 2011 | 15 | 32 | 15 | 1 – 192 | RC | <500 μm | Ali et al., 2013 |
| Urban Guangzhou, China/ | 27 | 19 | 6.47 | <dl–211 | HHV | <500 μm | Wang et al., 2010 |
| e-waste-Guangzhou, China/ 2008/2009 | 39 | 84.9 | 20 | nd–998 | HHV | <500 μm | Wang et al., 2010 |
| 23 provinces across China/ 2010 | 81 | 11 | 2.5 | 0.21- 220 | RC (brush sampling | n.a | Qi et al., 2014 |
| Trang Minh,Vietnam/ 2008 | 10 | n.a | 17 | 5.2–97 | RC | n.a | Tue et al., 2013 |

GM = geometric mean, n.a = not available

**Table 1.12: Summary of concentrations (ng/g) of DBDPE in house dust, sampling method (Researcher-collected (RC) or household vacuum (HHV)) and dust particle size analysed**

| City, Country/Sampling year | N | Average | Median | Range | Sampling method | Particle size | Reference |
|---|---|---|---|---|---|---|---|
| Boston, US/ 2006 | 19 | 138 (GM) | 201 | <10.0-11,070 | RC | <500 μm | Stapleton et al., 2008 |
| California, US/ 2010-2011 | 27 | 96.5 (GM) | 161 | <2.60-1,650 | HHV | <150 μm | Brown et al., 2014 |
| Toronto, Canada/ 2013 | 23 | 95 | 15 | <dl-2,060 | RC | <500 μm | Venier et al., 2016 |
| Bloomington, United States/ 2013 | 20 | 367 | 148 | <dl-3140 | RC | <500 μm | Venier et al., 2016 |
| Birmingham, UK/ 2006-2007 | 30 | 270 | 24 | <dl-3400 | RC | <500 μm | Harrad et al.,2008a |
| Antwerp, Belgian, 2008 | 39 | 303 | 153 | <20–2,470 | RC | <500 μm | Ali et al., 2011a |
| Munich, Germany/ n.a | 20 | 323 | 146 | 47–1,570 | HHV | <63 μm | Fromme et al., 2014 |
| Stockholm, Sweden/ 2012 | 27 | 21 (GM) | 12 | <0.4 -2,200 | RC | n.a. | Newton et al., 2015 |
| Stockholm, Sweden/ 2009-2010 | 27 | 145 (GM) | 150 | 43–1,500 | RC | n.a. | Sahlström et al., 2015 |
| Brno, Czech Republic/ 2013 | 20 | 20 | 4.7 | <dl-114 | RC | <500 μm | Venier et al., 2016 |
| Kuwait city, Kuwait/ 2011 | 15 | 510 | 220 | 40 – 2,175 | RC | <250 μm | Ali et al., 2013 |
| Faisalabad, Pakistan/ 2011 | 15 | 130 | 90 | 2.5 – 465 | RC | <500 μm | Ali et al., 2013 |
| Urban Guangzhou, China/ 2008-2009 | 27 | 5194 | 2733 | 100–47,000 | HHV | <500 μm | Wang et al., 2010 |
| e-waste-Guangzhou, China/ 2008-2009 | 39 | 171 | 63.1 | 13.5–1,144 | HHV | <500 μm | Wang et al., 2010 |
| Trang Minh,Vietnam/ 2008 | 10 | n.a | 220 | 31–1,600 | RC | n.a | Tue et al., 2013 |
| 23 provinces across China/ 2010 | 81 | 1100 | 280 | <dl-16,000 | RC (brush sampling) | n.a | Qi et al., 2014 |

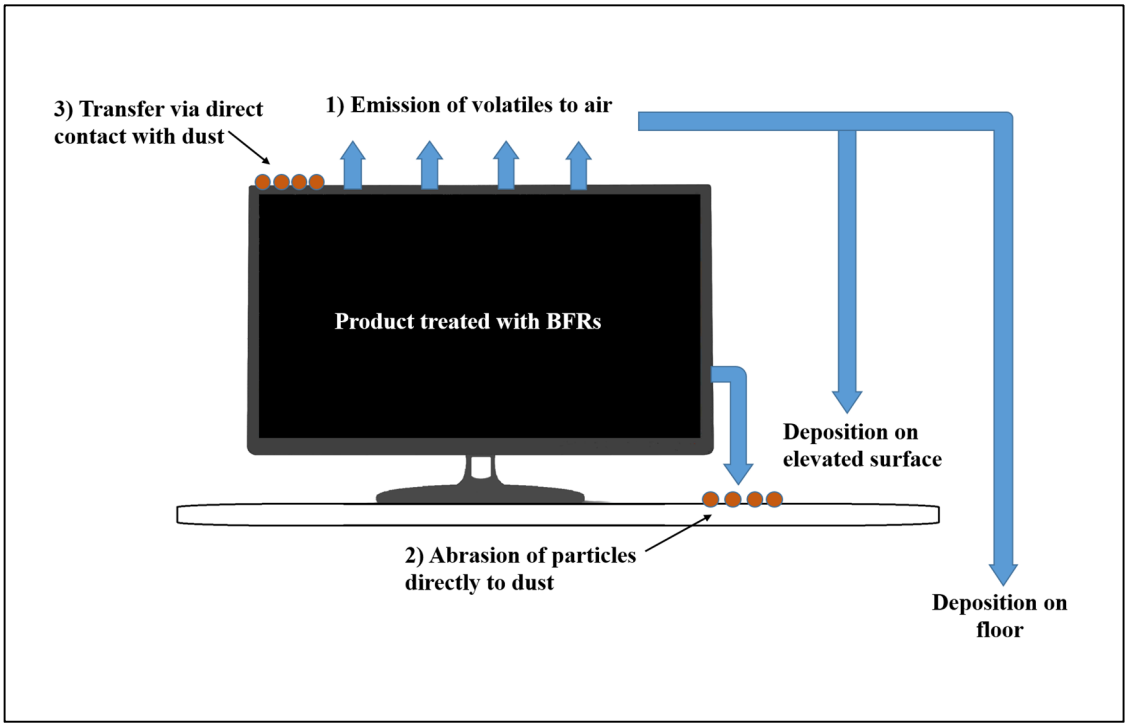
GM = geometric mean, n.a = not available

## 1.7 Pathways of BFR migration into indoor dust

It has been hypothesised that BFRs migrate from products into indoor dust via three mechanisms which are: (1) BFR sorption to dust particles after volatilisation from treated products, (2) physical transfer via abrasion from products in the form of particles or/and fibres, and (3) direct contact between dust and the surface of products (Rauert et al., 2014a).

Vapour pressure ($V_P$) and the octanol air partitioning coefficient ($K_{OA}$) are important factors influencing BFR fate and behaviour in indoor microenvironments. As mentioned in section 1.5.1.2, brominated flame retardants that have higher vapour pressure are expected to migrate to the environment via evaporation. By using emission test chambers, Kemmlein et al., 2003 determined the emissions of selected organic pollutants (including BFRs) from selected consumer products under constant environmental conditions. The study concluded that Penta-BDEs volatilisation occurred from both foam and electronics, with emission strength increased at higher temperatures. Partitioning between the gas phase and particulate phase is an important influence on the relative importance of different human exposure routes to BFRs. Such partitioning is controlled by the octanol-air partition coefficient ($K_{OA}$) (Weschler and Nazaroff, 2010). Due to their small surface area to mass ratio, particles and airborne aerosols act as sinks for organic species in the indoor environment (Morawska and Salthammer 2003). The deposition of SVOCs like BFRs to settled dust is thus to be expected (Fromme, 2012). However, this explanation is an inadequate explanation for the highly elevated concentrations in some dust samples of lower vapour pressure compounds like BDE-209 (See chapter 5, section 5.3.3). Webster et al., (2009) used scanning electron microscopy to investigate PBDEs in dust suggesting "that the BDE-209 was transferred to dust via physical processes such as abrasion or weathering". By using an in-house test chamber with forensic microscopy techniques, Rauert et al., (2014b) identified in dust, some fibres containing high concentrations of HBCDDs that arose as a result of abrasion of a treated curtain. This study suggested that "the abrasion migration pathway is a likely source of the elevated concentrations of BFRs" in some dust samples (Rauert et al., 2014b). Direct contact between dust and the surface of treated products is likely to be driven by a combination of dust properties, physicochemical properties of the BFR and the contact time between the dust and the treated products (Rauert et al., 2014a). Figure 1.5 illustrates the three hypothesised routes of BFR migration from the treated product to indoor dust.

**Figure 1.5: Mechanisms of BFR migration from treated product to indoor dust (modified from Rauert et al., 2014a)**




## 1. 8 Method of analysis for PBDEs and NBFRs in dust samples

In order to determine a very low concentrations of chemicals, it is essential to reduce matrix complexity and employ an appropriate analytical method such as GC-MS or LC-MS. In general, techniques for the determination of BFRs in environmental samples adhere to the following series of operations: (1) extraction of the target compounds from the sample matrix, (2) isolation of the BFRs from co-extracted chemicals, (3) concentration of the sample, and (4) measurement using appropriate instrumental methods (Covaci et al., 2003; Guerra et al., 2011; Ionas and Covaci 2013)

### 1. 8.1 Extraction

The extraction procedure isolates the contaminants from the matrix and transfers them to an organic solvent. The extraction process is based on organic solvent extraction methods. These methods are determined by the solubility of the target compound in the extraction mixture, the accessibility of the extraction solvent and the time required for the extraction procedure. For BFR extraction from a solid material, solvents such as hexane, toluene, and dichloromethane are commonly used. Due to the wide range of BFR polarity, the best

extraction recoveries were found when a polar and non-polar solvent mixture was used (Covaci et al., 2003, Ionas and Covaci 2013).

The most common extraction techniques for analysing BFRs in dust samples are Soxhlet extraction, accelerated solvent extraction (ASE), microwave-assisted extraction (MAE), and ultrasonic extraction (Covaci et al., 2003). Soxhlet extraction is one of the oldest methods of solid sample pre-treatment. The main principle of this method depends on the extraction of organic components in the solid sample by repeated extraction using a volatile organic solvent, by refluxing in special glassware that allows the extraction process to be repeated many times. Despite many advantages of this method, the main disadvantages are the long extraction times required (typically 4-24 h) and high solvent volumes required (Jensen, 2007). However, soxhlet has been used in a large number of laboratories to extract PBDEs and NBFRs from indoor dust (Gevao et al., 2006; Takigami et al. 2009; Wang et al., 2010; Zheng et al., 2011; Stapleton et al., 2014; Kefeni et al., 2014).

Ultrasonic extraction extracts chemicals from solid matrices by mixing with an organic solvent and subjecting the matrix: solvent mix to ultrasonic vibration. Energy is introduced into the sample by means of an ultrasonic bath into which the sample plus solvent is immersed (Webster, 2006). Recently an ultrasonic extraction method has been widely used to extract BFRs and NBFRs from dust samples due to the small volumes of solvents and short processing time required (Ali et al., 2011a; 2011b; Van den Eede et al., 2012; Shoeib et al., 2012; Dodson et al., 2012; Sahlström et al., 2012; Zhu et al., 2013; Ionas and Covaci, 2013; Cao et al., 2015; Kuang et al., 2016).

ASE extraction is a new technique introduced in 1995 by Dionex Corporation. It is fully automated technique that combines elevated temperatures and pressures with liquid solvents. The temperature in this technique is normally above the boiling point of the extraction solvent(s), which requires high pressure to keep the solvent in the liquid state during the extraction process. The processing time in ASE is between 15 and 25 min with consuming only 15–50 mL of solvent for each sample (Peterson et al., 2007). This method has been widely used to extract PBDEs and NBFRs from solid matrices such as indoor dust (Stapleton et al., 2005; 2008; Harrad et al., 2008a; 2008b; Abdallah et al.2008; Allen et al., 2008; Muenhor and Harrad, 2012; Stapleton et al., 2012; Harrad et al., 2016)

### 1.8.2 Clean-up and fractionation

Complex solvent extracts of samples require further purification before they can be subjected to chromatographic analysis. In order to reduce the sample complexity and obtain sufficiently clean extract of BFRs for chromatographic-mass spectrometric analysis, a combination of non-destructive and destructive clean-up methods are applied. This requires dividing the extract into more than one fraction depending on the polarity of the target compounds, which can be achieved by eluting BFRs from an SPE cartridge (a variety of different sorbent materials are used) with different solvents of increasing polarity (Ionas and Covaci, 2013). Silica gel, alumina, and Florisil are the most common sorbent materials, while a mix of non-polar solvents such as n-hexane and polar solvents such as acetone, ethyl acetate, dichloromethane, methanol, n-butyl chloride and diethyl ether as dipole solvents are most commonly used. Since PBDEs are resistant to strong acids, lipid removal is often effected by elution through sulfuric acid-impregnated silica gel (Guerra et al., 2011). Recently, clean-up methods used for determination of BFRs in indoor dust have been optimised using the principles above. PBDEs and DBDPE are eluted with n-hexane, with EH-TBB, BEH-TEBP and BTBPE eluted with polar solvents using activated silica (Ali et al., 2011b), deactivated silica (Sahlstrom et al., 2012) or Florisil (Van den Eede et al., 2012). In subsequent steps, acid treatment of the non-polar solvent fraction is achieved either via elution through acidified silica (Ali et al., 2011b; Van den Eede et al., 2012) or via liquid:liquid partitioning against concentrated sulfuric acid (Sahlstrom et al., 2012). To ensure that acid-labile BFRs are not degraded via these latter steps, EH-TBB, BEH-TEBP and BTBPE should not be subjected to acid treatment (Sahlstrom et al., 2012; Ionas and Covaci, 2013).

### 1.8.3 Instrumental analysis

BFRs are analysed by GC-MS and or LC-MS (gas or liquid chromatography coupled to mass spectrometry) depending on the polarity of the target analytes (Abdallah, 2014). Both GC-EI-MS and GC-ECNI-MS (electron ionisation – EI, and electron capture negative ionisation – ECNI) are the common analytical techniques applied for analysing BFRs in dust samples (Guerra et al., 2011). The highest sensitivity was obtained by GC–ECNI-MS, while GC–EI-MS was the most selective technique (Covaci et al., 2011; Cristale and Lacorte, 2013). Table 1.13 summarises the analytical methods employed over the last six years for the analysis of BFRs in indoor dust samples.

**Table 1.13: Summary of analytical methods used over the last 6 years for the determination of BFRs in indoor dust**

| Compounds | Extraction | Clean-up | Detection | Reference |
|---|---|---|---|---|
| EH-TBB, BEH-TEBP, BTBPE, DBDPE, TBBPA-DBPE and HCDBCO | (1) Shaking with 2 mL Hex/Ace (3:1, v/v). (2)Ultrasonication for 5 min followed by centrifuge at 3500 rpm (2 times) | (1) Activated silica cartridge, elution with 10 mL Hex (fraction1; HCDBCO and DBDPE), then 10 mL DCM (fraction 2; EH-TBB, BEH-TEBP, BTBPE and TBBPA-DBPE). (2) Fraction 1 to acid silica, and fraction 2 to Florisil, elution with 5 mL Hex, then 5 mL DCM. | GC/ECNI-MS | Ali et al., 2011b |
| PBDEs, EH-TBB, BEH-TEBP, BTBPE, DBDPE and HBCDs | Ultra sonication with 15 mL DCM for 30 min (2 times) | (1) Deactivated silica and $Na_2SO_4$ cartridge, elution with 30 mL Hex (fraction1; PBDEs and DBDPE), then 10 mL 5% DEE in Hex (fraction 2; EH-TBB, BEH-TEBP and DBDPE), then 10 mL 50% DEE in Hex (fraction 3; HBCDs). (2) Fraction 1 treated with $H_2SO_4$ and fraction 2 eluted with 12 mL Hex: DCM 1:1 v/v in aminopropyl silica | GC/ECNI-MS and only LC/MS for HBCDs | Sahlström et al., 2012 |
| PBDEs, EH-TBB, BEH-TEBP, BTBPE, DBDPE, HCDBCO, HBCD and OPFRs | (1) Shaking with 2 mL Hex/Ace (3:1, v/v). (2)Ultra sonication for 5 min followed by centrifuge at 3500 rpm (2 times) | (1) Florisil cartridge, elution with 8 mL hex (fraction1; PBDEs, EH-TBB, BTBPE, DBDPE, HCDBCO and HBCDs), then 10 mL EA (fraction 2; BEH-TEBP and HBCDs). (2) Fraction 1 eluted with 10 mL Hex: DCM (1:1, v/v) in acidified silica cartridge | GC/ECNI-MS for fraction1, GC/EI-MS for fraction 2, and LC-MS/MS for HBCDs | Van den Eede et al., 2012 |

**Table 1.13: Continued.**

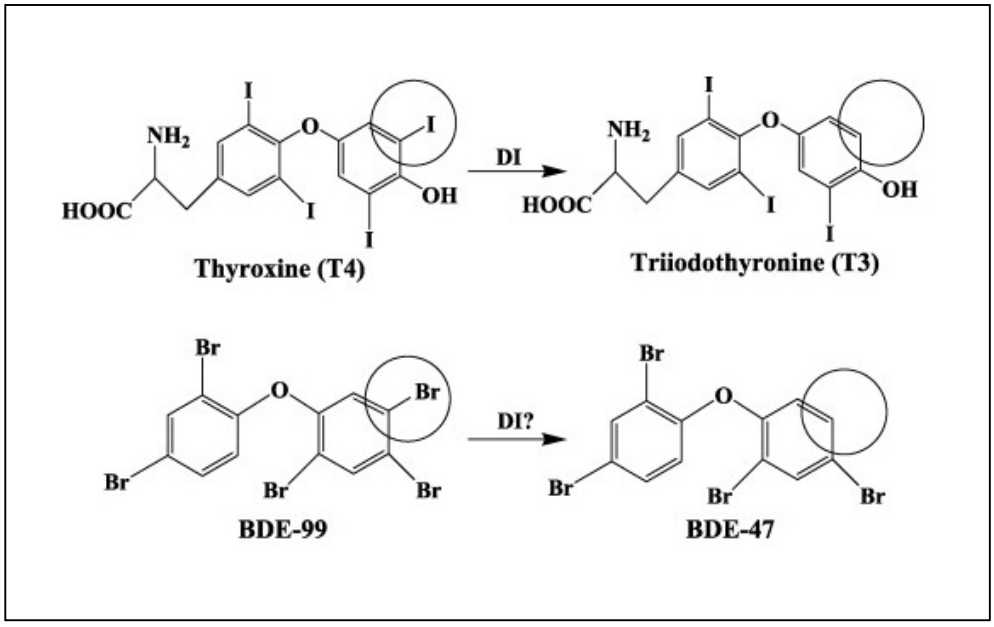
| Compounds | Extraction | Clean-up | Detection | Reference |
|---|---|---|---|---|
| PBDEs, EH-TBB, BEH-TEBP, HBCDs, TBBP-A, OPFRs | (1) Shaking with 2 mL Hex/Ace (3:1, v/v). (2)Ultrasonication for 5 min followed by centrifuge at 3500 rpm (2 times) | Underivatized silica cartridge , elution with 8.5 mL Hex (fraction1; PBDEs and non-polar NBFRs), then 8 mL of n-butyl chloride (fraction 2; HBCDs, TBBP-A and BEH-TEBP), then 8 mL EA (fraction 3, PFRs), then 8 mL MeOH (fraction 4, compounds more polar than PFRs) | GC/ECNI-MS and GC/EI-MS only, LC-MS/MS for HBCDs and TBBPA | Ionas and Covaci, 2013 |
| PBDEs, EH-TBB,BEH-TEBP, BTBPE, DBDPE, PBEB, other NBFRs and OPFRs | (1) Shaking with 10 mL EA/cyclohexane (5:2, v/v). (2)Ultrasonication for 10 min followed by centrifuge at 300 rpm (2 times) | Florisil cartridge (5 g), elution with 30 mL EA/cyclohexane (5:2, v/v) | GC-EI-MS/MS | Cristale and Lacorte, 2013 |
| PCBs, PBDEs, PAHs, and NBFRs (included PBEB, EH-TBB, BEH-TEBP, BTBPE and DBDPE) | ASE with 95%:5% hex: DCM at 100 1C and1500 psi | (1)A glass column of silica gel and $Na_2SO_4$, elution with DCM/Hex (1:1, v/v). (2) Transferred to a gel permeation chromatography (GPC) autosampler | GC-MS in multiple ion detection modes (MID) | Brown et al., 2014 |
| PBDEs, NBFRs (included PBEB, BTBPE and DBDPE), TBBPA and HBCDs | no application | Mixture of (0.5 g dust and 0.05 Florisil) applied in SPE glass column filled with glass wool and 1 g Florisil, elution with 10 mL Hex: DCM, 15:85, v/v (fraction1; non-polar compounds), then 3 mL of DCM followed by 3 mL of mixture of DCM: MeOH 50:50, v/v and 10 mL of MeOH (fraction 2; polar compounds) . | GC/ECNI-MS and GC/EI-MS for PBDEs and NBFRs LC-MS/MS for the rest. | Lankova et al., 2015 |

## 1.9 Toxicology and health effects of PBDEs and NBFRs

In 1973, an incident in Michigan led to the identification of PBBs (polybrominated biphenyls) as a highly toxic chemical. During this incident, accidental contamination of cattle feed affected animals. Weight loss, decreased milk production, weakened resistance to infection, infertility and abortion were the main symptoms observed in the animals. Farmers whose food supply derived from these animals showed many other health symptoms after several months (Chanda et al., 1982; ATSDR, 2004). This horrific incident was the start of the investigation into the potential toxic effects of brominated flame retardants. In addition, because of the large volume production scale of BFRs and their structural resemblance to other well-known contaminants such as DDT and PCBs, BFRs have become a cause for concern (Darnerud, 2003). Based on the available experimental data generated from studies on animals such as rats, mice and rabbits, fish as well as bacterial tests, PBDEs have been classified as toxic compounds (Birnbaum and Staskal 2004; USEPA, 2006; 2008a; 2008b; 2008c; NICNAS, 2007; EFSA, 2012; European Commission, 2012). The majority of laboratory studies that have investigated the distribution and metabolism of BFRs, are based on oral exposure with limited studies based on high-dose inhalation or dermal exposure.

A number of studies on PBDEs have focused on the commercial mixture of Penta-BDEs and individual congeners particularly, BDE-47 (USEPA, 2008a), BDE-99 (USEPA, 2006) and BDE-153 (UAEPA, 2008b), as they are the most commonly measured in human tissues and are likely associated with higher toxicity in animal studies compared with the other congeners. Effects on thyroid gland function have also been linked strongly with exposure to Penta-BDE due to the similarity in chemical structure between thyroxine and BDE-99. *In vitro* and *in vivo* in common carp hepatic tissue, (Noyes et al., 2010) investigated the similarity between the conversion of Thyroxine (T4) to T3 by deiodinase (DI) enzymes in cells and the reductive dehalogenation of BDE-99 to BDE-47 as shown in Figure 1.6.

**Figure 1.6: The similarity between BDE-99 and Thyroxine (Noyes et al., 2010)**




Dunnick and Nyska (2009), investigated liver toxicity in rats and mice after oral exposure to lower molecular weight PBDEs (BDE-47, BDE-99, BDE-100, and BDE153). The study found that, in addition to increases in liver cytochrome levels and liver lesions, the most important parameter for Penta-BDE toxicity was the increase in liver weights, which occurred at 5 mg/kg above in rats and 50 mg/kg and above in mice. This suggested that after long-term exposure, liver may be a target organ for carcinogenesis processes (Dunnick and Nyska, 2009). In addition to their hepatotoxicity and effects on thyroid function (Noyes et al., 2010; Turyk et al., 2008; Chevrier et al., 2010), the most important potential Penta-BDE health effects of concern appear to be endocrine disruption (Meeker and Stapleton, 2010), neurodevelopmental effects (Herbstman et al., 2010) and effects on a reproductive system (Main et al., 2007; Akutsu et al., 2008). Estimated half-lives in humans (total body) were 2-3 years for BDE-47, BDE-99, BDE-100, and BDE-154, and 4-6 years for BDE-153, assuming gastrointestinal absorption of 86–96% (Geyer et al., 2004), while estimated half-lives in human serum were 11–18 day for deca BDEs and 37–91 days for octa BDEs (Thuresson et al. (2006). The long estimated half-lives of Penta-BDE augments concern about their human health effects.

It has been suggested a Tier 1 (4 screening- levels evaluation-hazard, exposure, risk and data needs) assessments of the potential health risk to children and prospective parents associated

with exposure to the commercial Octa-BDE. Among toxicity studies on Octa-BDEs, the most important end points in animal bioassays are in the liver, which included microscopic changes and increased liver weight, in addition to disruption in thyroid hormone and decrease in maternal and foetal body weight (VCCEP, 2003). Moreover, the EU risk assessment recommended Octa-BDE to be classified as "Toxic" substance due to possible risk of impaired fertility and harm to the unborn child (European Commission, 2012). Furthermore, animal studies suggested that Octa-BDE might bioaccumulate in adipose tissue (European Commission, 2012).

For Deca-BDE, Rice et al., (2007) tested locomotor activity of male and female mice after a daily oral dose of 0, 6, or 20 mg/kg Deca-BDE. The study found that after 20 mg/kg/day exposure locomotor activity declined over the course of the 2-hour assessment. In addition, a dose-related reduction in serum thyroxine levels appeared in males but not in females. "These effects suggest that Deca-BDE is a developmental neurotoxicant that can produce long-term behavioural changes following a discrete period of neonatal exposure" (Rice et al., 2007). Another study (Tseng et al., 2006) reported that the most serious effects of postnatal BDE-209 exposure of the male mouse to resulted in decreasing epididymal sperm functions. Yang et al., (2014b) investigated the toxicological effects of BDE-209 on female rats, found that, due to the high accumulation of BDE-209 in lipid, ovary, kidney and liver, and alternation in urine from the exposed rats, BDE-209 health risk might be of concern. Another study (Mariani, et al., 2015) on key neurodevelopmental molecules in foetal mouse concluded prenatal exposure to realistic concentrations of BDE-209 induces weakness in the central nervous system, suggesting a potential risk of toxicity in development foetal human. Li et al., (2014) investigated the carcinogenic potential of BDE-209 on human embryonic kidney cells, found a significant change in the gene expression profiles of cells treated with BDE-209. The study suggested that BDE-209 has a broader toxicity to disruption of thyroid hormone-related biological processes.

Monitoring of BFR in human populations provided data on toxicity. One epidemiological study suggested that prenatal PBDE exposure has negative effects on neurodevelopment. Herbstman et al. (2010) showed that children (12-48 and 72 months) who had higher levels of BDE-47, -99 and -100 in their cord blood performed less well in tests of mental and physical development. To investigate the associations between exposure to PBDEs and

thyroid hormone (TH) during pregnancy, as TH plays an important role in the normal foetal brain development, Chevrier et al., (2010), determined, 10 PBDE congeners, free thyroxine (T4), total T4, and thyroid-stimulating hormone (TSH) in serum samples from 270 pregnant women. The study found that concentrations of ΣPBDEs (BDEs 28, 47, 99, 100, and 153) were inversely associated with TSH levels. The study suggested that exposure to PBDEs during pregnancy may have implications for maternal health and foetal development (Chevrier et al., 2010).

Mankidy et al. (2014), investigated effects of NBFRs on steroidogenesis in primary porcine testicular cells. The study suggested that EH-TBB did not affect sex steroid production in this cell model, while greater production of the sex hormones testosterone and estradiol was observed at the highest concentrations of BEH-TEBP. Endocrine and reproductive effects of BFRs in animals have led researchers to investigate the associations between BFRs in house dust and hormone levels in men. Egloff et al. (2011) tested the toxicity of BTBPE and DBDPE in chicken embryos found, a dose-dependent, changes in the relative messenger RNA (mRNA) was observed in the embryonic livers. Johnson et al. (2013) concluded that exposure to Penta-BDEs, BTBPE and EH-TEBP in indoor dust may be leading to endocrine disruption in men.

## 1.10 Human exposure to PBDEs and NBFRs

Numerous studies have shown the presence of PBDEs and NBFRs in many media pertinent for human exposure, such as: indoor air (Harrad et al., 2006; Allen et al., 2007; Wu et al., 2010; Cequier et al., 2014; Yu et al., 2015; Newton et al., 2015), food (Shi et al., 2009; Munschy et al. 2007; Liu et al., 2014; Zheng et al., 2016; Fernandes et al., 2016) and indoor dust samples (Wilford et al., 2005; Harrad et al., 2008a,b; Stapleton et al., 2008; 2012; Harrad and Abdallah, 2011; Wang et al., 2010; Ali et al., 2012; Sahlstram et al., 2015; Cristale et al., 2016; Harrad et al., 2016). In addition, several studies have shown the presence of PBDEs and NBFRs in human tissues such as human milk (Johnson et al., 2013; Zhou et al., 2014; Bramwell et al., 2014), serum (Ali et al., 2014; Stapleton et al., 2012), and hair and nail samples (Kang et al., 2011; Liu et al., 2015). Human exposure to BFRs is suggested to occur via a range of routes including: ingestion of indoor dust via hand-to-mouth contact, ingestion of contaminated food including human milk, inhalation of BFR contaminated indoor air and dermal exposure (USEPA, 2010; USEPA, 2011).

Several studies have linked environmental levels of BFRs to body burdens. To conduct an integrated assessment of PBDE exposure and human body burden, Toms et al., (2009b), analysed matched samples of human milk, indoor air and indoor dust. Significant correlations were found between the concentration of BDE-99 in air samples and human milk and a significant correlation between BDE-153 and BDE-183 in dust samples and human milk. In another study, the same authors (Toms et al., 2009a) reported that PBDE levels are higher in children's blood serum (2-5 years old) than in adults and infants. Serum sample analysis observed that BDE-47, -99, -100 and -153 concentrations increased from 14± 3.4 ng/g lipid for children aged 0-6 months to 51 ± 36 ng/g lipid for children 2.6-3 years old, before decreasing to 9.9 ± 1.6 ng/g lipid in the 31–45 years old age group. In addition, Sjödin et al., (2008b) evaluated the correlation between human exposure to PBDEs and BB-153 with demographic information, such as age, sex and race by analysis of serum samples. The study found that there is no significant difference in the least square geometric mean by gender. However, there was a linear decrease with age ($p$ = 0.01) from 27.9 ng/g lipid in 12-19 years old to 20.4 ng/g lipid in ≥ 60 years old.

Inhalation and dermal exposure have been considered a minor source of exposure, while food consumption and ingestion of indoor dust are the major exposure routes. In the UK, Abdallah et al. (2008) reported that estimated exposure via dust ingestion for HBCDDs and TBBPA exceeded that via air inhalation. According to the same study, dust ingestion contributed 63-75% of daily exposure to HBCDD for toddlers and 24-28% for adults. Abdallah et al estimated that dust ingestion contributed 90-97% of exposure to TBBP-A for toddlers and 34-56% for adults respectively. The exposure of Americans to PBDEs was evaluated by Lorber, (2008). The study concluded that among all the exposure pathways (inhalation, water and food ingestion, and ingestion and dermal contact with house dust), house dust ingestion accounted for 82%. Food intake was estimated about 1.3 ng/kg/day from all PBDEs intakes (7.7 ng/kg) for adults. For NBFRs, Qi et al., (2014) found NBFR (EH-TBB, BEH-TEBP, BTBPE and DBDPE) exposure via dust ingestion was 3.8-14 times higher than dermal exposure.

### 1.10.1 Human exposure to PBDEs and NBFRs via indoor dust ingestion

Dust is defined as "solid particles formed by crushing or other mechanical breakage of a parent material, larger than about 0.5 μm" (Morawska, 2004). According to the United States Environmental Protection Agency, indoor settled dust is defined as "particles in building

interiors that have settled onto objects, surfaces, floors, and carpeting. These particles may include soil particles that have been tracked or blown into the indoor environment from outdoors as well as organic matter" (USEPA, 2011). Dust particles represent a good indicator of indoor contamination and act as a sink for semivolatile compounds (Morawska and Salthammer, 2003). Concentrations of BFRs in indoor dust are associated with higher body burdens in some (but not all) studies and hand-to-mouth activity may be a significant pathway, particularly for younger children (Harrad et al., 2008a: 2008b;2010b; Lorber, 2008; Roosens et al., 2009; Abdallah and Harrad 2009; Stapleton et al., 2012; Qi et al., 2014; Hoffman et al., 2015). In addition, it has been reported that people spend from 80% to more than 90% of their time indoors (Morawska and Salthammer, 2003).

A large number of studies indicated a positive relationship between BFR concentrations in human tissues and house dust. Wu et al., (2007) analysed PBDEs in indoor dust samples from 46 houses and human milk sampled from 46 first-time mothers living in these houses. A significant positive correlation was found between PBDEs (not including BDE-209) concentrations in house dust and breast milk ($r = 0.76$, $p = 0.003$). Another study (Coakley et al., 2013) investigated the relationship between human milk and indoor dust (mattress and floor), and found a positive correlation ($p < 0.05$) between breast milk and mattress dust concentrations for BDE-47, BDE-153, BDE-154, and BDE-209 and between breast milk and floor dust for BDE-47, BDE-183, BDE-206, and BDE-209. Stapleton et al., (2012) found that PBDE concentrations in indoor dust were highly correlated with matched serum samples. The study concluded that socioeconomic status, age and breastfeeding were significant predictors of PBDE exposure. In addition, Johnson et al., (2010) highlighted a strong correlation between Penta-BDE levels in matched indoor dust and serum samples for adults of both genders. Moreover, Kang et al. (2011) found a significant positive correlation between concentrations of BDE-183 in matched samples of indoor dust and human hair. Another study (Tang et al., 2013), reported a positive correlation ($p < 0.05$) between concentrations of BDE-47 and BDE-99 in human hair and indoor dust, but no correlation for other PBDE congeners. In addition, significant positive associations were found between indoor dust concentrations of Penta-BDEs, Octa-BDE, BTBPE and BEH-TEBP and hormone levels in men (Johnson et al., 2013). Differences between the BFR exposure of children and adults have been highlighted by Fischer et al., (2006). This study reported that within the same family, the youngest child had the highest concentration of PBDEs and the highest exposure from house dust. PBDE

concentrations in serum samples taken from the children were 2-5 fold higher than in their parents. For example, BDE-47 serum concentrations were 32, 60, 137 and 245 ng/g lw for father, mother, child and toddler respectively (Fischer et al., 2006). According to Lorber, (2008), the intake dose of total PBDEs is an estimated 7.7, 49.3, 14.4 and 9.1 ng/kg/day for adults, and children within the 1-5, 6-11, and 12-19 year age groups respectively.

As mentioned in section 1.10, dust represents an important pathway for human exposure to BFRs (Abdallah et al. 2008; Lorber, 2008; Qi et al., 2014). In addition to these studies. Harrad et al., (2006) showed that dust ingestion contributed an estimated 37% and 69% of UK overall exposure to $\Sigma_6$tri-hexa-BDEs of adults and toddlers respectively. These estimates were evaluated under a "typical" dust ingestion scenario. In Canada, dust ingestion contributed 14% and 80% of overall daily ΣBDE exposure of both adults and toddlers respectively (Wilford et al., 2005). In China, Wang et al., (2010), reported that BFR exposure assessments via dust ingestion were much higher than for other routes such as inhalation, consumption of fish and human milk, and mouthing of toys.

### 1.10.2 Factors influencing PBDEs and NBFRs concentrations in indoor dust

Due to the complex composition of indoor dust and the wide range of physicochemical properties of indoor contaminants, numerous factors influence the types and the level of pollutants that are associated with dust particulates. The adsorption and cohesion of these pollutants to the dust particles depends on the size and type of these particles (Maertens et al., 2004). In addition, the location of the sample, time of sampling, dust sampling method and surface loading are important factors affecting the levels of pollutants in indoor dust. Furthermore, the quantity and identity of these pollutants depends on the mechanism via which pollutants transfer from the source to indoor dust, the strengths of indoor sources and the ventilation rate (Harrad et al., 2010a)

#### 1.10.2.1 Within-room and within-building spatial variations

Assessments of human exposure to chemical pollutants via dust ingestion require knowledge about locations where people spend their time and thus come into contact with such pollutants. However, few studies have investigated spatial variability (variations in dust contamination taken at the same time from different locations within the same microenvironment) of BFR dust contamination within a given microenvironment. Variability in concentrations of PBDEs,

DBDPE and TBE (1,2-bis(2,4,6-tribromophenoxy ethane) in indoor dust was studied for the first time by (Harrad et al., 2008a) in the UK. From three homes and two offices, 5 floor dust samples were collected on the same day from different locations in one room. The study revealed high relative standard deviations (RSD) in BFR concentrations compared with those calculated from replicate analyses of a dust standard reference material (SRM2585). The RSD for Σtri-hexa-BDE concentrations in the five rooms studied ranged between 28% and 80%. It has been suggested that in order to obtain a representative sample, dust samples must be collected from the entire surface of the room studied. This is considered to reflect the relationship between contamination and potential emission sources which are a part of a microenvironment's characteristics (Harrad et al., 2008a). Another study by the same authors (Harrad et al., 2009) tested within-room spatial variability in concentrations of HBCDs from six microenvironments (3 homes and 3 offices). In this study, some rooms showed little spatial variability (RSD = 7% - 8%) in HBCDs concentrations, while others displayed large variability (RSD = 19% - 100%). In one room, the study identified a TV as the main source of HBCDs, as HBCD concentrations in dust from inside the TV were highly elevated and levels in floor dust decreased with increasing distance from the TV. Muenhor and Harrad, (2012) also tested within-room spatial variability in PBDE contamination of dust. From six separate rooms (four from one house and two from another), samples (2- 4) were taken from different areas in each room. In one room, the study found that the PBDE concentrations in an area close to putative PBDEs sources (TV, laptop, and sofa) exceeded significantly those in area 2 m away from the same sources. Cequier et al., (2014) compared BFR concentrations in floor dust and dust from elevated surfaces (shelves, tables, chairs, electronics, etc.) collected from the same residences. The study found that median concentrations of BFRs in elevated surface dust exceeded those in floor dust. According to Cequier et al, the reason is due to the direct contact between the settled dust and surface of products likely to contain BFRs. In addition, floor dust may contain amounts of materials that were tracked from outdoor that are less likely to be contaminated by BFRs. Spatial variations in BFR concentrations were also investigated in vehicles. Harrad and Abdallah (2011) tested the within-vehicle spatial variability of PBDEs, HBCDs, and TBBP-A in UK cars, finding that BFR concentrations in dust samples from passenger cabins exceeded significantly ($p < 0.05$) those in trunk dust. In addition, comparison of concentrations in dust taken from four different seating areas, showed concentrations of TBBP-A, BDE-154, -206, -207, -208, and -209 in dust samples from the front seats exceeded significantly those in the rear seats.

A small number of studies have investigated within-home spatial variability in BFR dust contamination. From 20 homes in Boston, the USA, Allen et al., 2008 analysed PBDEs in dust samples collected from the living room and bedroom of each home. Concentrations of Penta- and Deca-BDE congeners were, on average, significantly higher in the living room than those in the bedroom. The study suggested that this uniformity between the two rooms at the same home was expected as Penta- and Deca-BDE are room-specific sources. Similarly, Muenhor and Harrad, (2012), found PBDE concentrations in separate rooms of the same home can vary quite markedly. In one home, average ΣPBDE concentrations in the bedroom (430±180 ng/g) exceeded substantially those in the other bedroom (170±340 ng/g) from the same home. In another home, ΣPBDE average concentrations in the bedroom (80±57 ng/g) were markedly higher than those in the other bedroom (37±21 ng/g). The study suggested that in one house, the differences in PBDE concentrations between the rooms may be attributable to the presence of a carpet in one room while the other room had a bare wooden floor (Muenhor and Harrad, 2012). Very recent studies reported no significant differences between the living room and bedroom in BFR concentration in indoor dust. In Canada, Venier et al., (2016), found no statistical differences between PBDE and NBFR concentrations in dust from the living room and bedroom in the same home (n= 10). The study suggested that the sources of the target FRs are widespread and their influence is mixed between rooms in the same house. Finally, Kuang et al., (2016) investigated concentrations in dust of PBDEs and selected NBFRs in 30 homes in the UK, finding no significant differences ($p > 0.05$) between BFR concentrations in the living room and bedroom.

#### 1.10.2.2 Temporal and seasonal variation

Depending when a given room is sampled, substantial temporal variability (variations in dust contamination taken from the same area of the same room over different periods) for PBDE concentrations in indoor dust was reported. Harrad et al., (2008a) found that over a 9 month period, substantial temporal variability in PBDE concentrations was observed in three rooms studied. The RSD values ranged between 52% and 156% for Σtri-hexa-BDEs and between 58% and 166% for BDE-209. This was attributed to changes in the contents of the rooms. For example, substantial increases in BDE-209 and Σtri-hexa-BDE concentrations were observed when a new fabric bed cover and curtains were fitted during the sampling period. The concentrations rose from 7,200 to 43,000 ng/g for BDE-209 and from 2.7 to 150 ng/g for Σtri-hexa-BDEs (Harrad et al., (2008a). This implies that temporal variations in BFR

concentrations could identify the emission source of these pollutants. Within three rooms of three UK homes, Harrad et al., (2009) examined HBCDs concentrations over 9-10 months. RSD values were 27%, 42% and 190% for ΣHBCDs in the three homes investigated. The low RSD value (27%) was attributed to an absence of obvious changes in room contents, while in the second home, an RSD of 42% was attributed to the temporary removal of a TV, implying that the TV was the emission source. In the third home, a high RSD value (190%) was attributed to the introduction of a new rug (Harrad et al., 2009). In another UK study, Muenhor and Harrad (2012), monitored floor dust in 14 different areas for eight months, finding substantial variation in Σtri-hexa-BDE concentrations. The study reported that the RSD values observed (ranging between 16-61% for BDE-47 and 17-120% for BDE-99) exceeded substantially those obtained from 12 replicate analyses of SRM 2585 (9.3 and 5.9%) for BDE-47 and -99 respectively). The study found concentrations of ΣPBDEs were higher in samples from rooms containing putative sources of these compounds, particularly in the areas closest to such sources. For instance, in one of the bedrooms studied, replacement of the bed after the first month of monitoring caused ΣPBDE concentrations to decrease from 276 to 46 ng/g (Muenhor and Harrad 2012).On the other hand, Allen et al., (2008) reported no significant changes in concentrations of Penta- and Deca-BDE over the eight month period. This may be because of very limited changes in the contents of the room.

Seasonal variability between colder (September-March) and warmer (March-September) months was also studied by (Muenhor and Harrad 2012) in indoor dust from 14 areas. The study found that while in seven sampled areas, average concentrations of ΣPBDEs in the colder months was higher than in warmer months, the reverse was observed in the other seven areas. The study attributed the lack of clear seasonal variation to the greater volatile emissions of BFRs in warmer months, being offset by higher ventilation during the same periods. Seasonal variability in PBDEs (tri-deca-BDE) was investigated by Yu et al., (2012) in China during the four seasons. The study noted that PBDE concentrations were summer > winter > spring > autumn. The differences in concentrations between spring, summer, and winter were not statistically significant, however, in autumn, the concentrations were significantly lower than other seasons. Seasonal variation patterns in PBDE (tri-hepta-BDEs) and NBFR (EH-TBB, BEH-TEBP, BTBPE and DBDPE) concentrations in dust samples was studied by Cao et al., (2014b) in 3 offices in China over a 10 month monitoring period. The study revealed maximum: minimum concentration ratios were between 2 and 10,

implying the importance of the time of dust collection for exposure assessments. The RSD values of ΣPBDEs and ΣNBFRs were 28%, 87% and 66% for ΣPBDEs, and 19%, 84% and 33% for ΣNBFRs for the three offices. However, these two groups of BFRs were stable between March and December 2012. The order of BFR concentrations were winter > autumn > summer. (Cao et al., (2014b).

#### 1.10.2.3 Dust particle size and carbon contents

Various classifications have been used to define and specify dust particle size ranges. The most common classification defines particle mass ranges between 2.5 μm ($PM_{2.5}$) and 10 μm ($PM_{10}$) as the total suspended particles in the air, and particles with diameters > 30 μm as settled particles that are sedimented in the form of dust precipitation. Small dust particles include "skin flakes, fragments of hair, microorganisms, such as fungal spores and pollen, food crumbs, abrasion of textiles and fittings, sand, loam, clay, and soot" (Morawska, 2004), while larger dust particles may include plant debris, hair, and gravel. It is likely that different indoor environments have different compositions of dust. For example, dust from urban houses with pets and heavy abrasion of carpets will contain more organic materials than dust from kindergartens, which may contain a greater proportion of inorganic materials like sand and clay (Morawska, 2004). In general, indoor dust (suspended and settled) falls into a wide range of particle size fractions ranging from < 2.5 μm to over 2 mm (Morawska and Salthammer 2003). For settled dust exposure is presumed to occur via ingestion and dermal contact, while for suspended dust exposure is assume to occur via inhalation (Butte and Heinzow, 2002; Cao et al., 2012).

Regarding exposure via settled dust ingestion, a large and growing body of literature has investigated human exposure to BFRs via indoor dust using a disparate range of particle sizes, such as, < 63 μm (Kopp et al., 2012), < 75 μm (Xu et al., 2015), < 100 μm (Kang et al., 2011), < 125 μm (Wu et al., 2007), < 150 μm (Wilford et al., 2005; Shoeib et al., 2012; Whitehead et al., 2012), < 500 μm (Allen et al., 2008; Wang et al., 2010), 25-500 μm (Harrad et al. 2008a; 2008b; Muenhor et al., 2010; Brommer et al., 2012), < 1000 μm (Suzuki et al., 2006), < 2000 μm (Gevao et al., 2006) and all fractions (Takigami et al., 2008). However, for human exposure assessment, dust particles < 250 μm are considered of particular concern (USEPA, 2000; 2003; 2008d), as these have been proposed as those most likely to stick to hands and be ingested (Lioy et al., 2002; Ruby et al., 2012). For example, "House dusts of

different particle sizes < 246 μm adhered equally well to hands" (Que Hee et al. (1985). In addition, Kissel et al. (1996) found that soil particle adherence to hands was inversely correlated with particle size, directly with particle moisture content and independent of carbon content. For dry soil, particles > 250 μm displayed the lowest adherence to hands. Furthermore, it has been reported that increasing bioaccessibility was observed with decreasing particle size (Fang and Stapleton, 2014). Based on an expanding body of evidences, for assessment of incidental ingestion, TRW (Technical Review Workgroup for Metals and Asbestos) recommended moving from dust particles < 250 μm to < 150 μm. These evidences illustrate that the adhered dust is dominated by particles < 150 μm (USEPA, 2016).

Several studies have investigated distribution patterns of organic pollutants in settled indoor dust as a function of particle size. Early studies on polycyclic aromatic hydrocarbons (PAHs) and pesticides in indoor dust and airborne particles indicate that, due to the inverse relationship between particle size and specific surface area, levels of these pollutants increase gradually with decreasing particle size (Lewis et al., 1999; Sygiyama et al., 2000). The first study to investigate PBDE concentrations as a function of dust particle size was ten years later (Wei et al., 2009). By analysing four different dust fractions (250- 420 μm, 150-250 μm, 75-150 μm, and < 75 μm) in indoor dust (1 car and 2 homes), Wei et al. found that PBDE levels in car dust were inversely related to particle size, while they were comparable in homes. Limited studies since suggest BFR concentrations are influenced significantly by dust particle size. Kefeni et al., (2014) reported that of the PBDEs detected in dust particles < 250 μm from 2 homes and two offices; 93.4% were associated with particles < 150 μm. In a similar study, Chao et al., (2014) found no significant difference in concentrations of $\Sigma_{28}$PBDE in different particle sizes of house dust and electronic dust. Based on analysis of office dust particle size fractions, Cao et al., (2013) reported some variation in concentrations of PBDEs with particle size. Concentrations of tri-hexa PBDEs were highest in the 74-100 μm and 100-200 μm particle size fractions, those of hepta-PBDEs were greatest in 200-300 μm and 300-400 μm fractions, octa- and deca-PBDE concentrations peaked in particles < 50 μm, while 2-bis (2,4,6-tribromophenoxy) ethane (BTBPE) was highest in the 50-74 μm and 75-100 μm size range. Cao et al., (2014a) found that in several non-domestic microenvironments, BDE-209 showed higher levels in coarser particles in kindergartens (500-900 μm) and dormitories (900-2000 μm). Moreover, BFR concentrations did not increase constantly with decreasing particle size. Instead, the variation of concentrations with particle size was multi-modal, with the

highest levels associated with particle sizes around 900, 100, and 10 μm (Cao et al., 2014a). A later study revealed no significant variation in concentrations of HBCDs between different particle size fractions (Cao et al., (2015). Other studies have used forensic microscopy to show that the highest levels of BFRs are present in particles with different morphology, containing more fibre-like material (Wei et al., 2009; Cao et al., 2013).

As mentioned in section 1.7, particles and airborne aerosols act as sinks for organic species in the indoor environment. As lipophilic compounds, BFRs are usually expected to sorb to dust particles with higher organic carbon contents. Depending on the original source, which reflects the organic and inorganic composition, indoor dust falls into a wide range of organic contents ranging between 5% and 95%. For example, dust from kindergartens can contain higher abundances of inorganic materials compared with house dust from the residences of animal owners or carpeted floor homes (Morawska and Salthammer 2003). There are three basic forms of carbon that may be present in indoor dust, which are elemental, inorganic and organic carbon (USEPA, 2002). Inorganic carbon (IC) and total organic carbon (TOC) are commonly measured in indoor dust (Ferge et al., 2006).

#### 1.10.2.4 Sampling method and dust loading

Various approaches have been developed for collecting indoor settled dust samples. Dust sampling methods can be divided into passive and active techniques. Passive techniques involve use of dust fall plates, and simply letting suspended dust settle and accumulate for a given period of time. 99% of dust particles collected via this technique are < 50 μm. However, this technique is rarely used due to the long time required to obtain a sufficient quantity of indoor dust (Butte and Heinzow 2002; cited in Mercier et al., 2011). Active techniques include several approaches, which are surface wipes, sweeping and vacuuming (Maertens et al., 2004). A significant correlation was found between passive and active techniques for dust sampling for analysing pesticides in homes of farmers (Lemley, et al., 2002 cited in Mercier et al., 2011)

Wipe-sampling techniques are the original approach for indoor dust collection, which were commonly used after 1974. In these methods, samples were obtained by rubbing hard surfaces with disposable paper towels moistened with alcohol (USEPA, 1995). However, due to its insufficient capacity for collecting fine particles of dust (< 250 μm), wipe approaches are not

recommended by USEPA for Superfund lead risk assessments (USEPA, 2008d). However, this method was widely used to collect dust likely to adhere to hands. The wipe approach has been used by several studies to investigate the relationship between indoor dust and BFR metabolites in human tissues (Stapleton et al., 2012; 2014; Allen et al., 2013; Hoffman et al., 2015; Stephanie et al., 2016). The main advantages of the wipe method are that it is quick, easy, clean, involves minimal contamination and can be used for large-scale collection of samples in public health studies. However, the quantity of dust collected via this method is relatively small, and the weight of the wipe post-sampling may not be accurate due to the abrasion process (Mercier et al., 2011).

The vacuum cleaner is thus the most common approach used in collecting settled dust. The HVS3 (High Volume Small Surface Sampler) is a high-powered vacuum cleaner that has been validated by the US Environmental Protection Agency (USEPA) for measuring lead and several organic contaminants (pesticides, PAHs, and PCBs) in dust in carpets. In comparison with other methods, the HVS3 is the most accurate approach and strongly correlated with blood contaminant levels due to the small particles (< 5 μm) retained by the HVS3 (Sterling et al., 1999; Lioy et al., 2002). This method has been widely used, although it can be expensive, complicated and time-consuming (Mercier et al., 2011; USEPA, 2008d). Thus, commercial vacuum cleaners are widely used as an alternative to the HVS3.

By using a commercial vacuum cleaner, two approaches for dust collection are used in studies of indoor contaminants. One of these approaches involves householders providing the contents of their vacuum cleaners to the researchers (Harrad et al., 2006; Suzuki et al., 2006; Kopp et al., 2012; Shen et al., 2015; Cristale et al., 2016). Colt et al., (2008) compared the HVS3 method and the household vacuum sampling method and concluded that for detecting, ranking and quantifying the concentrations of pesticides and other chemicals in carpet dust, the household vacuum cleaner approach constitutes a reasonable alternative to HVS3. The principal advantages of the householder vacuum cleaner approach are that: it reflects indoor contamination from all rooms, it is cost-effective, a large quantity of dust can be obtained in at short time and it enhances donor compliance, by not requiring researchers to enter the home. However, dust collected by this approach may be contaminated by the inner part of the vacuum cleaner, thereby reducing the accuracy of this method. Moreover, spatial variability, temporal variability and dust loading cannot be assessed by this method, as the time and

locations covered by the sample are unknown. In addition, vacuum cleaner sampling rates will be variable (Harrad et al., 2010b). Another approach involves the use of a commercial vacuum cleaner by the researchers themselves by using standardized procedures and specific accessories such as socks inserted in the sampling train to retain dust (Brommer et al., 2012; Ali et al., 2013; Harrad et al., 2016), Soxhlet thimbles (Allen et al., 2008; Stapleton et al., 2012) and filters (Björklund et al., 2012; Thuresson et al., 2012; Newton et al., 2015). The main advantages of such researcher-collected dust approaches are that: it minimises contamination of the sample due to specific accessories which are replaced between taking each sample, and that it provides information about the specific time and specific location of collection of each dust sample, thereby facilitating study of within-room and within-home spatial and temporal variations in BFR concentrations. However, in comparison with the householder vacuum approach, this method is expensive and time-consuming, and may possibly hinder donor compliance as it requires entry of the researcher to the sampled microenvironment (Harrad et al., 2010b). Only two studies (Allen et al., 2008; Björklund et al., 2012) have investigated the variation between researcher-collected and household vacuum approaches for analysing PBDE in indoor dust, with their findings discussed in Chapter 6, section 6.3.3.

Any of the above approaches cannot be evaluated as effective in the context of exposure assessment without matching measurements of body burden (Allen et al., 2008). In this context, the “best” sampling method is the one that provides the most accurate reflection of what the room occupants are actually exposed to. For example, sampling dust from tables, shelves and high surfaces likely reflects adult exposure better than floor dust; with the latter a likely better indicator of the exposure of toddlers and pets (Dye et al., 2007 cited in Costa et al., 2008). Because there is no current universal standard method, Harrad et al., (2010b) instead recommended providing more details about sampling method when reporting results.

Human exposure estimates to BFRs via dust ingestion rely on the use of uniform values of dust ingestion rates regardless of the dust loading. This may not be correct. Despite a lack of data on how dust ingestion rates vary with dust loading, it is plausible that higher dust loadings will lead to increased dust ingestion rates. While this would suggest higher exposures in dustier rooms, it is also plausible that higher dust loadings will dilute BFR concentrations in dust, and it is not known how these two competing factors will impact on exposure. To date,

while three studies (Harrad et al., 2008a; 2009; Muenhor and Harrad 2012) have examined the evidence for such "dilution" of BFR concentrations in the dust at higher dust loadings; their findings are inconclusive. It has been hypothesised that, under certain conditions, “dilution” of BFR concentrations will occur at greater dust loadings. These conditions are: (a) BFR emissions remain constant through the monitoring period, and (b) the source of the dust and BFRs are independent – i.e. the main source of the BFR to dust is not direct abrasion of fibres or particles from a source material (Harrad et al., 2008a; 2009). Another study (Muenhor and Harrad, 2012), found no evidence for dilution of PBDE concentrations at high dust loadings.

#### 1.10.2.5 Microenvironment categories

While the majority of studies have focused on house dust; the contamination of indoor dust with BFRs has been evaluated in a variety of microenvironment categories such as offices (Cao et al., 2014b), classrooms (Harrad et al., 2010a; Ali et al., 2011a), hotels (Takigami et al., 2009), cars (Thuresson et al., 2012) and airplanes (Allen et al., 2013). Various levels of BFRs were found between dusts from various microenvironments. Suzuki et al., (2006) reported that PBDE concentrations in house dust in Japan were 140-3,000 ng/g (median 700 ng/g), while those in office dust were 260-20,000 ng/g (median 1,800 ng/g). In the UK, Harrad et al., (2008a) investigated BFRs in different microenvironments and found that concentrations of BDEs 47, 99, 100, and 154 in car dust exceeded significantly ($p < 0.05$) those in dust from homes and offices. Average concentrations of PBDEs and DBDPE in homes, offices and cars were 260,000, 31,000 and 340,000 ng/g PBDEs and 270, 170, and 400 ng/g DBDPE respectively. Another study (Abdallah et al., 2008) reported that HBCD concentrations in cars > homes > public microenvironments > offices, while TBBPA concentrations in public microenvironments > homes > offices > cars. In Hong Kong, Kang et al., (2011) found that concentrations of PBDEs in work places (397- 40,236 ng/g) are much higher than those in homes (685-18,383 ng/g). In Germany, Brommer et al., (2012) reported that PBDE concentrations in cars and offices were significantly higher than those in houses. In Nigeria, Harrad et al., (2016) found PBDE concentrations in cars were generally higher than in offices and homes. BDE-49, BDE-154 concentrations in car dust samples were significantly higher than those in both homes and offices, while BDE-197 concentrations in cars were significantly higher than those in homes only. It has been noted that higher concentrations of BFRs in indoor dust are associated with the abundance of electronic

equipment PUF-containing furniture in various microenvironments, which has been confirmed via within-room, and within-building spatial and temporal variation in contamination (Rauert et al., 2014a).

## 1.11 Estimated daily intakes of BFRs via dust ingestion

Inhalation and ingestion of particulate-bound BFRs in indoor environments have been considered as direct pathways of exposure to these chemicals. Exposure to BFRs via indoor dust is currently estimated as a multiple of the concentrations of these chemicals present in indoor dust and the dust ingestion rate. This exposure is then compared to the tolerable daily intake to evaluate the potential health risk. Evaluations of exposure via dust ingestion usually assume 100% absorption of intake and dust ingestion rates of 20 and 50 mg/day (average/"typical") and 50 and 200 mg/day (high-end) for adults and toddlers respectively (Jones-Otazo et al., 2005). It is important to note however that "due to the large uncertainties in these default values, and the small contribution of inhalation to the total house dust intake, a total daily intake of house dust of 50 and 100 mg/day is used for adults and children, respectively" (Oomen et al., 2008). The estimated daily intakes (EDIs) of BFRs can be evaluated by comparison with their corresponding reference dose (RfD) (Table 1.13)

**Table 1.14: Reference-dose (RfD) values of PBDEs and NBFRs (USEBA, 2006; 2008a; 2008b; 2008c; Hardy et al. 2008)**

| Target compound | RfD (ng/kg bw/day) | Target compound | RfD (ng/kg bw/day) |
|---|---|---|---|
| BDE-47 | 100 | EH-TBB | 20,000 |
| BDE-99 | 100 | BTBPE | 243,000 |
| BDE-153 | 200 | BEH-TEBP | 20,000 |
| BDE-209 | 7,000 | DBDPE | 333,333 |

It has been indicated that human exposure to BFRs via ingestion of indoor dust is highly variable due to the wide range in human body burdens, thereby "support(ing) the hypothesis that ingestion of household dust may account for the observed international differences in human body burdens" (Harrad et al., 2008b). Harrad et al., (2008b) estimated daily intakes of tri-hexa-BDEs and BDE-209 via dust ingestion in Canada, New Zealand, UK and the USA. The study observed that for tri-hexa-BDEs, higher exposure was found in North America, while for BDE-209, higher exposure was found in the UK. The "typical" estimates were 12,

1.9, 1.2, and 33 tri-hexa-BDEs ng/day for adults and 31, 4.8, 2.9 and 82 tri-hexa-BDEs ng/day for toddlers in Canada, New Zealand, UK and the USA respectively. For BDE-209, the "typical" exposure estimates were 11, 56, 26 BDE-209 ng/day for adults and 28, 140, 65 BDE-209 ng/day for toddlers in Canada, UK and the USA respectively. In China, exposure estimates to BFRs and PBDEs for inhabitants of e-waste-impacted areas were 37.0 and 92.5 ng/day for PBDEs, and 3.00 and 7.52 ng/day for other BFRs for adults and toddlers respectively (Wang et al., 2010).

## 1.12 Objectives and hypotheses

Indoor settled dust has been recognised as an important pathway of human exposure to brominated flame retardants via ingestion. In addition, concern about these chemicals has risen because of available evidence about their toxicity. However, assessment of human exposure to BFRs via contact with indoor dust is rendered uncertain because of a lack of knowledge about factors such as: (a) spatial and temporal variation in BFR contamination of dust and (b) the type of dust sampled (elevated surface or floor, particle size sampled, and the sampling collection method). The main purpose of this thesis is to investigate the most important factors affecting human exposure assessments via indoor dust ingestion. The principal objectives were thus to:

1. Investigate within-room and within-home spatial variability in concentrations of PBDEs and NBFRs in indoor dust.

2. Monitor within-room and within-home temporal variability, and seasonal variability in concentrations of PBDEs and NBFRs in indoor dust.

3. Study the distribution pattern of PBDEs and NBFRs in different particle size fractions of indoor dust.

4. Compare the influence of dust sampling approach and dust surface loading on concentrations of PBDEs and NBFRs in indoor dust.

5. Estimate human exposure to PBDEs and NBFRs via dust ingestion in Basrah, Iraq and evaluate the implications of elevated surface dust and floor dust on both adults and toddlers exposure following different scenarios.

**The hypotheses tested were that:**

- Human exposure assessments of PBDEs and NBFRs via dust ingestion are affected by within-room and within-home spatial variability.

- Temporal variability in PBDEs and NBFRs concentrations in indoor dust could influence human exposure assessments via dust ingestion.

- BFR concentrations will increase with decreasing particle size fraction, which will affect substantially on exposure assessment.

- Concentrations of PBDEs and NBFRs in dust from elevated surfaces will exceed significantly those in floor dust from the same microenvironment.

- Differences in BFR concentrations between elevated surfaces and floor dust or between different particle size fractions could be attributed to differences in the total organic carbon (TOC) contents.

- BFR concentrations in researcher-collected dust (RCD) will be different from those in the household vacuum dust (HHVD) samples.

- Under certain conditions, as a consequence of a “BFR dilution effect”, a significant negative correlation between the logarithms of BFR concentrations and dust loadings is expected.

# CHAPTER 2

## METHODOLOGY

## 2.1 Summary

In order to address the hypotheses and the aims outlined in chapter 1, sampling methods and analytical techniques were developed and modified from previous studies to facilitate assessment of the main factors affecting human exposure assessments of BFRs via dust ingestion. Sampling was conducted according to two main approaches. Bulk indoor dust samples were collected mainly according to a standard protocol (Harrad et al., 2008a), while a small number of samples were obtained from vacuum cleaner bags from householders. In addition, elevated surface dust samples were also collected using a standard protocol. The number, type and location of house dust samples depended on the research question(s) taking such samples was designed to address - e.g. the influence on BFR concentrations in dust of spatial and temporal variability, sampling method and dust properties. The dust extraction method was based on a method developed elsewhere (van den Eede et al. 2012; Ali et al., 2011b) using modified internal standards. In this project, a new clean-up method was optimised based on an understanding of the physicochemical properties of and literature relating to the determination of PBDEs and NBFRs. The amounts of solvent and sorbent materials were adapted to enable the determination of the PBDEs and NBFRs in the same dust sample via a single GC-MS instrumental method. To ensure the validity of the optimised method, procedures for its validation and quality assurance/ quality control measures were implemented.

## 2.2 Chemicals

Native and labelled PBDE and NBFR standards were purchased from Wellington Laboratories Inc. Guelph, Canada as stock solutions in iso-octane, while BDE-209 and $^{13}C$ BDE-209 were purchased as stock solutions in nonane. The recovery determination (syringe) standard PCB-129 in hexane was purchased from Qmx Laboratories, UK. The purity of all standards > 98%. Table 2.1 gives the abbreviations, names and concentrations of these chemicals.

**Table 2.1: Abbreviation, name and concentration of the standards (target compounds, internal standards (IS) and recovery determination standards (RDS)) used in this project**

| Abbreviation | Compound | Concentration |
|---|---|---|
| BDE-28 | 2,4,4'-tribromodiphenyl ether | 50 ng/µL |
| BDE-47 | 2,2',4,4'-tetrabromodiphenyl ether | 50 ng/µL |
| BDE-77 | 3,3',4,4'-tetrabromodiphenyl ether (IS) | 50 ng/µL |
| BDE-99 | 2,2',4,4',5-pentabromodiphenyl ether | 50 ng/µL |
| BDE-100 | 2,2',4,4',6-pentabromodiphenyl ether | 50 ng/µL |
| BDE-128 | 2,2',3,3',4,4'-hexabromodiphenyl ether (IS) | 50 ng/µL |
| BDE-153 | 2,2',4,4',5,5'-hexabromodiphenyl ether | 50 ng/µL |
| BDE-154 | 2,2',4,4',5,6'-hexabromodiphenyl ether | 50 ng/µL |
| BDE-183 | 2,2',3,4,4',5',6-heptabromodiphenyl ether | 50 ng/µL |
| $^{13}$C BDE-209 (MBDE-209) | $^{13}$C-Decabromodiphenyl ether (IS) | 25 ng/µL |
| BDE-209 | 2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether | 50 ng/µL |
| PBEB | Pentabromoethylbenzene | 50 ng/µL |
| EH-TBB | 2-ethylhexyl-2,3,4,5-tetrabromobenzoate | 50 ng/µL |
| $^{13}$CBTBPE (MBTBPE) | $^{13}$C 1,2-bis(2,4,6-tribromophenoxy)ethane (IS) | 50 ng/µL |
| BTBPE | 1,2-bis(2,4,6-tribromophenoxy)ethane | 50 ng/µL |
| $^{13}$C BEH-TEBP (MBEH-TEBP) | $^{13}$C bis(2-ethyl-1-hexyl) tetrabromophthalate (IS) | 50 ng/µL |
| BEH-TEBP | Bis(2-ethyl-1-hexyl)tetrabromophthalate | 50 ng/µL |
| DPDBE | Decabromodiphenylethane | 25ng/µL |
| PCB-129 | 2,2',3,3',4,5-Hexachlorobiphenyl (RDS) | 100 ng/µL |

Ethyl acetate (EA), Acetone (Ac), *n*-Hexane, dichloromethane (DCM), iso-octane, phosphoric acid and sulfuric acid were purchased from Fisher Scientific UK Ltd. All solvents used were of HPLC analytical grade.

Silica gel (pore size 60 A˚, 70-320 mesh) was purchased from Sigma Aldrich, Switzerland, anhydrous sodium sulfate was obtained from Sigma Aldrich, USA, and Florisil® (particle

size 60-100) was acquired from Fluka, USA. The NIST standard reference material (SRM 2585, “Organic Contaminants in House Dust”) was purchased from the National Institute of Standards and Technology (NIST) Gaithersburg, MD, USA. Sodium bicarbonate was purchased from Nacalai Tesque, Japan, and sucrose (analytical reagent grade) was purchased from Fisher Scientific, UK. ISOLUTE amino propyl columns, SPE cartridges and frits were purchased from Biotage (Uppsala), Sweden. Acid impregnated silica (44%, w/w) was prepared as described elsewhere, (Method 1614, USEPA, 2007). Activated Florisil® was prepared by baking at 450 ˚C for 1 hour, cooling and subsequent cleaning with *n*-hexane (1 cycle extraction by Accelerated Solvent Extraction) and stored (for no more than one week) until use in a sealed pre-cleaned glass bottle.

## 2.3 Sampling and sample preparation

UK dust samples (n=320) were collected from Birmingham and Iraqi dust samples (n=36) were collected from Basrah, both are the second largest cities in terms of populace in the UK and Iraq. From urban houses, sample collection was carried out in between 2013 and 2015, using two sampling approaches. The first approach used a handheld vacuum cleaner (DIRT DEVIL-DDMHH1-1100W), according to a clearly defined standard protocol (Harrad et al., 2008a). 1 $m^2$ of carpeted floor was vacuumed for 2 min and, in case of bare floor, 4 $m^2$ for 4 min using 25 μm pore size nylon sample socks (Allied Filter Fabric Pty Ltd, Australia) that were mounted in the furniture attachment tube of the vacuum cleaner. As there was no existing defined sampling protocol for elevated surfaces, the standard protocol was adapted for this purpose. Elevated surfaces (typically between 50-150 cm height) were vacuumed for 2-4 min depending on the surface area. The elevated surface areas sampled included the most common, such as: chairs and sofas, desks, shelves and tables. After sampling, socks were closed with a twist tie, sealed in plastic bags and stored at −20 ˚C. Before sampling, the furniture attachment and the vacuum tubing were cleaned thoroughly using isopropanol-impregnated disposable wipes and dried between collections. To reflect as far as possible, actual human exposure to BFRs, the sampling method was conducted under normal room conditions. Participants were requested to not vacuum their houses (floor and elevated surfaces) for at least 3 days prior to sampling. A second sampling approach involved householders providing the contents of their domestic vacuum cleaner bags.

For investigating spatial and temporal variability in BFR contamination of indoor dust, dust samples (n=238) were collected every month for nine months, from three homes (H1, H2 and H3) in Birmingham, UK. Each month, from each home, nine dust samples from three rooms (R1, R2, and R3) were collected. R1 is the living room, R2 an adult bedroom, and R3 a study room, except for H3, where R3 was a child's bedroom. From each room, one sample was collected from elevated surfaces (ES), in addition to two samples from two different positions of the floor (F1, F2) (Figures, 3.1, 3.2 and 3.4, in Chapter 3). Due to the low dust loadings encountered on elevated surfaces in the homes sampled, 2-3 elevated surface samples from the same room were combined to yield 4 elevated surface samples over the 9 month sampling period. Hence, while each floor dust sample represents a single month, each elevated dust sample represents either 2 or 3 months.

To investigate the influence on BFR concentrations in dust of dust particle size and organic carbon content; every month dust samples were collected from 5 homes in Birmingham, UK, for 4 months in two homes, and for 5 months in three, comprising one elevated surface (ESD) and one floor (FD) dust sample from each home from living room and bedrooms. A total of 46 dust samples were collected during the sampling period. To provide sufficient dust mass, each sample used for this aspect of the study comprised dust collected from e.g. elevated surfaces in the same home for 4-5 months combined. Aliquots of each of these 10 samples were then fractionated into three particle size fractions P1 (125-250 μm), P2 (63-125 μm), and P3 (25-63 μm), which were analysed alongside the bulk non-fractionated sample (BD), thereby affording a total of 40 samples for this strand of the investigation.

To investigate the influence of sampling method on BFR concentrations in dust, 36 dust samples were collected from 12 homes in Birmingham, UK. From each home, 1 dust sample was obtained from the vacuum cleaner bag for that home; in addition, two samples of floor dust were collected by the standard protocol outlined above from the same house: one from the living room and a second from the bedroom.

Finally, to provide the first evaluation of the exposure for the Iraqi population, 36 dust samples were collected from 18 homes in Basrah, Iraq. In each home, one dust sample was collected from elevated surfaces (ESD) with another one collected from the floor (FD), following the

standard protocol outlined above. Table 2.2 summarises the samples taken for different strands of the study.

**Table 2.2: Summary of dust samples taken**

| Investigated factor | No. of homes | No. of collected samples | No. of analysed samples |
|---|---|---|---|
| Spatial and temporal variability | 3 | 238 | 193 |
| Particle size and organic carbon content | 5 | 46 | 40 |
| Sampling method | 12 | 36 | 36 |
| Exposure for the Iraqi population | 18 | 36 | 36 |
| Total | 38 | 356 | 305 |

Dust samples for all 3 UK studies (Table 2.2) were collected from different homes. At the outset of the sampling campaign, information on house age, room dimensions, occupants and time spent in each room was recorded. In addition, at the time of sample collection, information was recorded about: numbers and types of putative sources like electronic devices, foam-filled furniture and floor material, ventilation system, house cleaning method and any changes in room contents or positioning within the room sampled (Appendix 1). One field blank sample was obtained from each home; consisting of 1 g of pre-extracted anhydrous sodium sulfate placed on an aluminium foil sheet and vacuumed as if it were a dust sample.

Prior to analysis, all dust samples were passed through a pre-cleaned, *n*-hexane rinsed 250 μm mesh testing sieve (UKGE Limited, UK), covered with the lid and shaken for 3-5 min, to ensure a better sample homogeneity. For samples designed to investigate the influence on BFR concentrations of dust particle size and organic matter content; following initial sieving to 250 μm as above, three different size sieves (63, 125, and 250 μm) were placed over each other from smallest (bottom) to greatest (top) and sieving conducted for 5-7 min. This process yielded three different indoor dust fractions: 125–250, 63–125, and 25-63 μm. After settling for 30 sec, sieved dust samples were transferred into clean *n*-hexane rinsed glass jars and stored at 4 ˚C until analysis.

## 2.4 Sample extraction

Sample extraction was performed according to Ali et al., (2011b) and Van den Eede et al., (2012) with minor modifications. In a 12 mL glass centrifuge tube, an accurately weighed aliquot of dust sample (typically 45-125 mg) was spiked with a mixture of internal standards (20 ng of BDE-77, BDE-128, MBTBPE, MBEH-TEBP, and 40 ng of MBDE-209) in isooctane. These internal standards were chosen as they elute in the same fraction as the investigated pollutants during the clean-up fractionation procedure, and do not coelute with them under the GC conditions employed. Table 2.3 lists the target compounds and their corresponding internal standards and masses added per sample.

**Table 2.3: Target compounds and the amount of their corresponding internal standards**

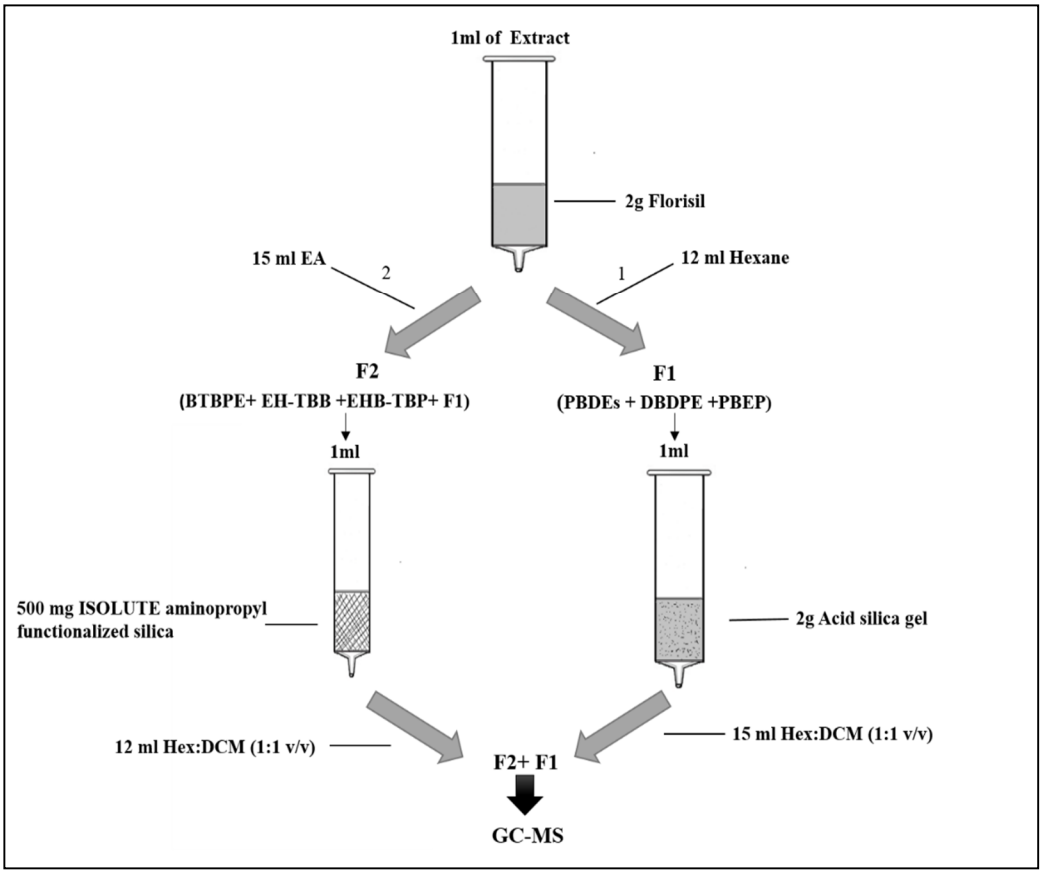
| Target compounds | IS | IS amount added per sample (ng) |
|---|---|---|
| BDE-28 | BDE-77 | 20 |
| PBEB | | |
| BDE-47 | | |
| BDE-100 | | |
| BDE-99 | | |
| BDE-154 | BDE-128 | 20 |
| BDE153 | | |
| BDE-183 | | |
| EH-TBB | MBTBPE | 20 |
| BTBPE | | |
| BEH-TEBP | MBEH-TEBP | 20 |
| BDE-209 | MBDE-209 | 40 |
| DBDPE | | |

Dust samples were extracted with 2 mL *n*-hexane: acetone (3:1 v/v), 2× (vortexed for 2 min, sonicated for 5 min) and centrifuged at 3500 rev/min for 5 min. The extraction process was repeated three times and after each repeat, the supernatant was separated. The combined extracts were evaporated to incipient dryness under a gentle nitrogen stream, resolubilised in 1 mL of *n*-hexane and vortexed for 1 min.

## 2.5 Extract purification (Clean-up procedure)

The concentrated extract was quantitatively transferred onto a SPE column packed with 2 g Florisil® that was prebaked and prewashed with *n*-hexane. Before the sample extract was applied, the column was conditioned with ~15 mL of *n*-hexane. Analytes were eluted in two fractions: fraction 1 (F1) (containing PBDEs, DBDPE and PBEB) was eluted with 12 mL of *n*-hexane, with fraction 2 (F2) (containing BTBPE, EH-TBB, and BEH-TEBP) eluted with 15 mL of EA. F1 was evaporated to 1 mL under a gentle nitrogen stream and transferred onto a 2 g 44% w/w acidified silica cartridge, pre-conditioned with 15 mL *n*-hexane prior to elution with 15 mL hex: DCM (1:1 v/v). F2 was evaporated to dryness under a gentle nitrogen stream, resolubilised in 2-3 mL *n*-hexane, before reduction in volume to 1 mL, and transfer onto an aminopropyl functionalised silica column (0.5 g, prewashed with 6 mL *n*-hexane), eluted with 12 ml hex:DCM (1:1 v/v) . F1 and F2 were combined and evaporated under nitrogen flow using a Turbovap (Biotage Turbo Vap® II) to dryness, before resolubilisation in 100 µL of iso-octane containing PCB-129 at 250 pg/µL ready for GC-MS analysis. Figure 2.1 summarises the clean-up method.

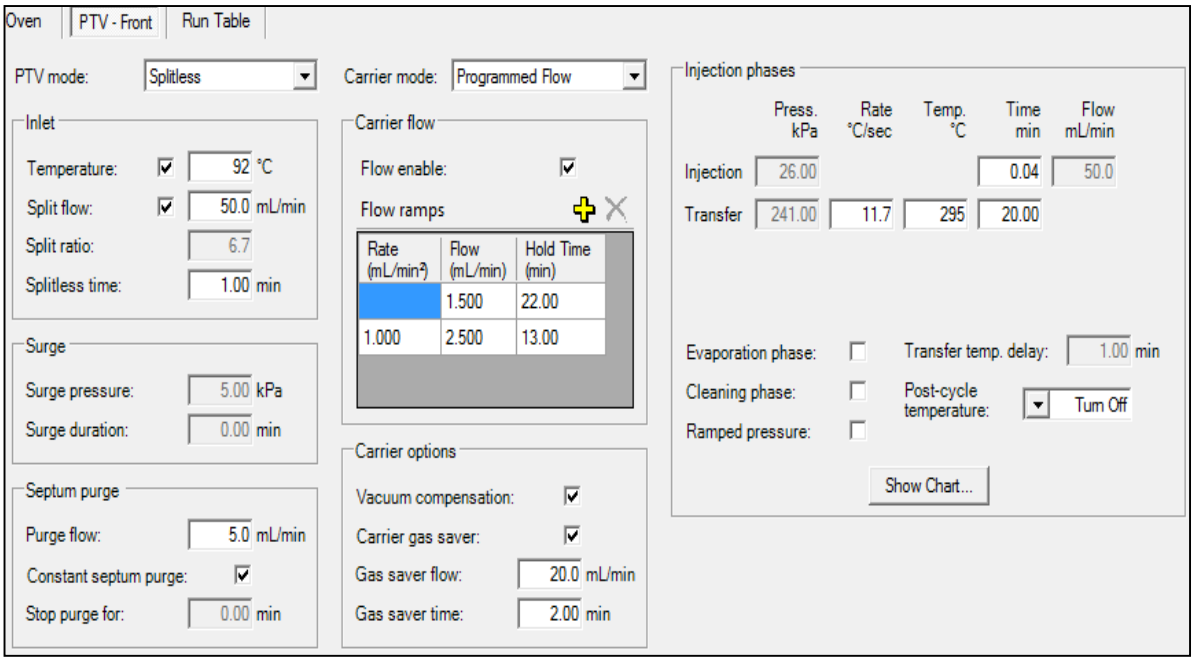
**Figure 2.1: The optimised clean-up procedure for dust samples**



## 2.6 GC-MS analysis method

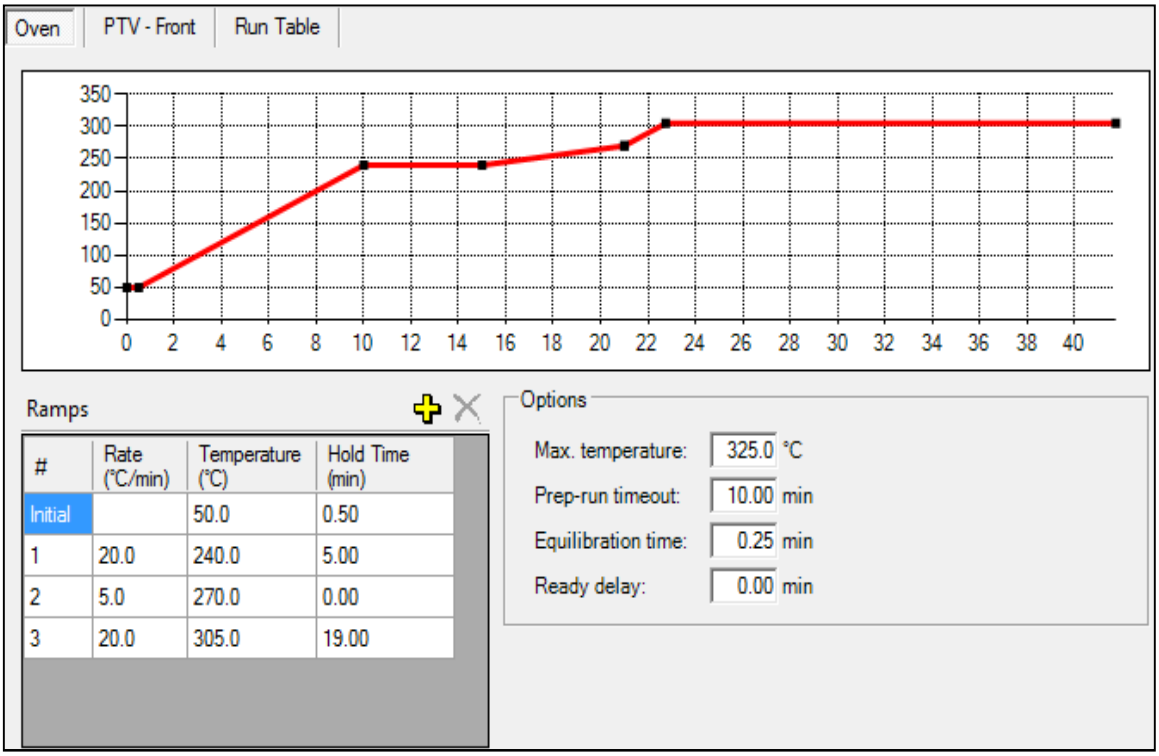
The analysis of PBDEs and NBFRs was performed using a gas chromatograph (GC) (Trace 1310 Gas Chromatograph) coupled to a mass spectrometer (MS) (ISQ Quadrupole MS); both (Thermo Fisher Scientific, USA). The GC was equipped with a programmable temperature vaporiser (PTV) injector and fitted with a capillary fused silica column (RESTEK, USA, 15 m x 0.25 mm inner diameter, 0.25 µm film thickness). 2 µL of purified extract were injected on the column. The inlet temperature was set at 92 ℃, split flow 50 mL/min, splitless time 1 min and purge flow 5 mL/min. The carrier mode was set on programmed flow at 1.5 mL/min, hold time 22 min, then 2.5 mL/min, hold time 13 min. Injection time was 0.04 min, transfer rate 11.7 ˚C /sec to 295 ˚C, hold time 20 min. Figure 2.2 illustrates the PTV method.

**Figure 2.2: PTV method for PBDEs and NBFRs analysis**



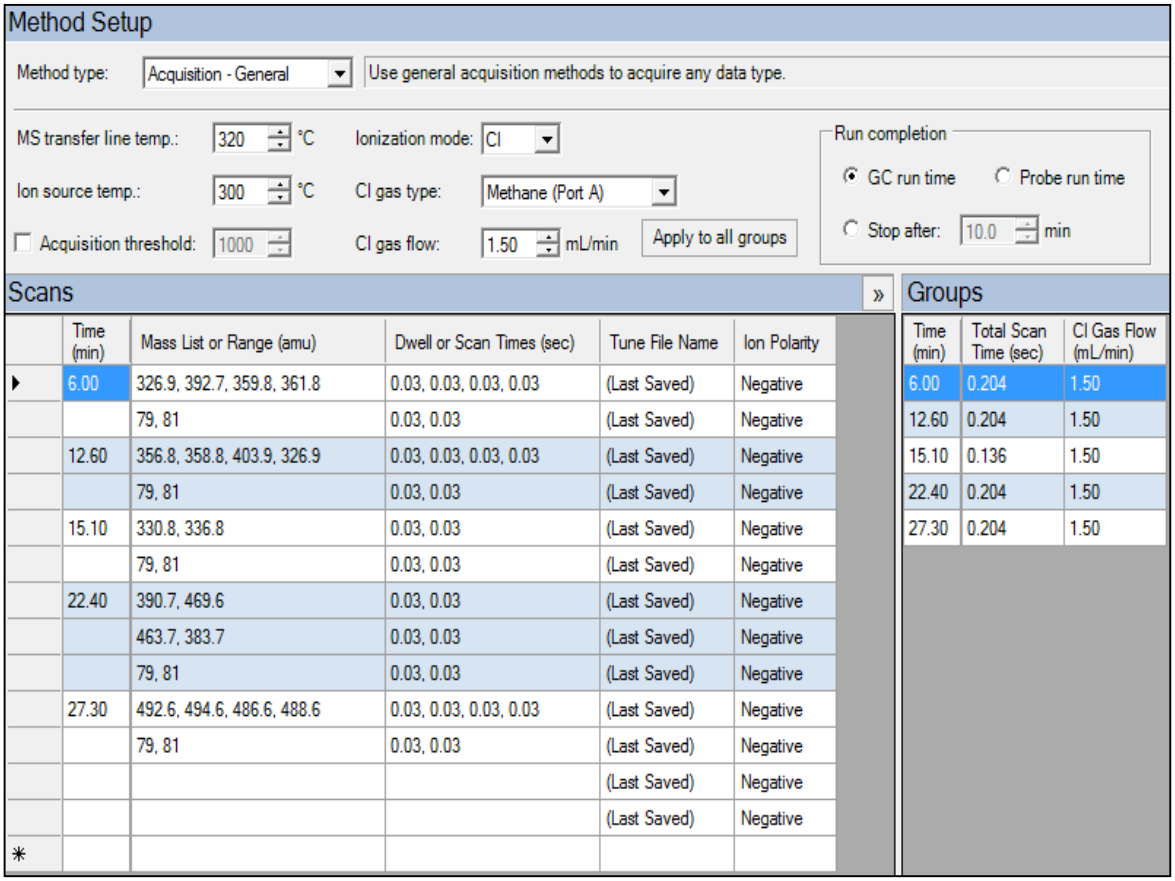
The GC oven temperature program was set at 50 ˚C for 0.5 min, ramp 20 ˚C/min to 240 ˚C, hold 5 min, ramp 5 ˚C/min to 270 ˚C, and ramp 20 ˚C/min to 305 ˚C, hold 19 min. Helium was used as a carrier gas with a flow rate of 1.5 mL/min. Figure 2.3 shows the GC temperature programme.

**Figure 2.3: GC temperature programme for PBDEs and NBFRs**




The MS was operated in the electron capture negative ion (ECNI) mode with methane used as standard reagent gas at a flow rate of 1.5 mL/min. The electron lens voltage was 15 V and emission current 50 µA. The ion source and transfer line temperature were 300 ˚C and 320 ˚C respectively. Detailed information about the MS analysis parameters and selected masses, are provided in figure 2.4.

**Figure 2.4: MS method for PBDEs and NBFRs analysis**




| Time (min) | Mass List or Range (amu) | Dwell or Scan Times (sec) | Tune File Name | Ion Polarity |
|---|---|---|---|---|
| 6.00 | 326.9, 392.7, 359.8, 361.8 | 0.03, 0.03, 0.03, 0.03 | (Last Saved) | Negative |
| | 79, 81 | 0.03, 0.03 | (Last Saved) | Negative |
| 12.60 | 356.8, 358.8, 403.9, 326.9 | 0.03, 0.03, 0.03, 0.03 | (Last Saved) | Negative |
| | 79, 81 | 0.03, 0.03 | (Last Saved) | Negative |
| 15.10 | 330.8, 336.8 | 0.03, 0.03 | (Last Saved) | Negative |
| | 79, 81 | 0.03, 0.03 | (Last Saved) | Negative |
| 22.40 | 390.7, 469.6 | 0.03, 0.03 | (Last Saved) | Negative |
| | 463.7, 383.7 | 0.03, 0.03 | (Last Saved) | Negative |
| | 79, 81 | 0.03, 0.03 | (Last Saved) | Negative |
| 27.30 | 492.6, 494.6, 486.6, 488.6 | 0.03, 0.03, 0.03, 0.03 | (Last Saved) | Negative |
| | 79, 81 | 0.03, 0.03 | (Last Saved) | Negative |
| | | | (Last Saved) | Negative |
| | | | (Last Saved) | Negative |

| Time (min) | Total Scan Time (sec) | CI Gas Flow (mL/min) |
|---|---|---|
| 6.00 | 0.204 | 1.50 |
| 12.60 | 0.204 | 1.50 |
| 15.10 | 0.136 | 1.50 |
| 22.40 | 0.204 | 1.50 |
| 27.30 | 0.204 | 1.50 |

The mass spectrometer was operated in selected ion monitoring (SIM) mode. BDE-28, PBEB, BDE-47, BDE-77, BDE-99, BDE-100, BDE-153, BDE-154, BDE-128, BDE-183 and DBDPE were monitored quantitatively using the bromine ion *m/z* 81 as they produce abundant stable ions *m/z* 81 and 79. In order to enhance selectivity, different ions were qualitatively monitored as listed in table 2.4. EH-TBB was monitored quantitatively using *m/z* 356.8 and qualitatively using 358.8. BTBPE and $^{13}$C-BTBPE were monitored quantitatively using *m/z* 330.8 and 336.8 respectively, with *m/z* 81 was monitored as qualitative ion. BEH-TEBP was monitored using 383.7 and 463.7, and $^{13}$C-BEH-TEBP was monitored using 390.7 and 469.6. BDE-209 was monitored using 486.6 and 488.6, while $^{13}$C BDE-209 was monitored using 492.6 and 494.6. In addition, the recovery determination standard PCB-129 was monitored using 359.8 and 361.8. Table 2.4 shows quantification ions, qualification ions and retention times monitored for target compounds, internal standards (IS) and the recovery determination standard (RDS). The quantification was performed using XCALIBUR software 2.2 SP1 (Thermo Fisher Scientific, USA).

**Table 2.4: Quantification and qualification ions (m/z), and retention time monitored for target compounds, internal standards (IS) and recovery determination standard (RDS)**

| Analyte | Quantification | Qualification | Retention time (min.) |
|---|---|---|---|
| BDE-28 | 81 | 326.9 | 10.02 |
| PBEB | 81 | 392.7 | 10.30 |
| PCB-129 | 359.8 | 361.8 | 10.60 |
| BDE-47 | 81 | 326.9 | 11.50 |
| BDE-77 | 81 | 326.9 | 12.22 |
| BDE-100 | 81 | 403.9 | 13.26 |
| BDE-99 | 81 | 403.9 | 13.95 |
| EH-TBB | 356.8 | 358.8 | 14.10 |
| BDE-154 | 81 | 330.8 | 16.47 |
| BDE-153 | 81 | 330.8 | 17.73 |
| BDE-128 | 81 | 330.8 | 21.05 |
| BDE-183 | 81 | 330.8 | 21.38 |
| $^{13}$C-BTBPE | 336.8 | 81 | 22.09 |
| BTBPE | 330.8 | 81 | 22.09 |
| $^{13}$C-BEH-TEBP | 390.7 | 469.6 | 22.79 |
| BEH-TEBP | 383.7 | 463.7 | 22.93 |
| $^{13}$C-BDE-209 | 492.8 | 494.8 | 31.24 |
| BDE-209 | 486.8 | 488.8 | 31.24 |
| DBDPE | 81 | 79 | 35.13 |

## 2.7 Quality Assurance/Quality Control and method validation

All glassware was cleaned by soaking them overnight in a detergent solution, followed by rinsing with tap water, and then deionised water. After washing, glassware and Pasteur pipettes were heated to 470 ˚C for 5 h. Before use, all glassware was rinsed with acetone and hexane. To avoid any degradation that may occur via exposure to light, glassware and the Turbovap instrument were covered with aluminium foil.

### 2.7.1 Instrument calibration

To assess the linearity of MS response, a full five point calibration was conducted. These calibration standards contained native analytes, internal standards and the recovery determination standard. Apart from the IS and RDS for which the concentration was a constant 200 pg $\mu L^{-1}$, calibration standards comprised PBDEs and NBFRs at different concentrations, Table 2.5 illustrates the exact concentrations and content of these calibration standards.

**Table 2.5: Concentration of target compounds, internal standard, and recovery determination standard in five levels calibration standard**

| Standard | BFR Native (pg/ µL) | DBDPE (pg/ µL) | IS (pg/ µL) | RDS (pg/ µL) |
|---|---|---|---|---|
| Std A | 25 | 50 | 200 | 200 |
| Std B | 50 | 100 | 200 | 200 |
| Std C | 200 | 400 | 200 | 200 |
| Std D | 500 | 1000 | 200 | 200 |
| Std E | 1000 | 2000 | 200 | 200 |

Good linearity was achieved with a correlation coefficient exceeding 0.996. In addition, these five standards are used to calculate relative response factors (RRFs) for each target compound. The RRF is defined as the instrument response for a unit amount of target compound (native) relative to the instrument response obtained for the same amount of the internal standard (IS). Equation 1.2 illustrates how RRFs were calculated.

$$RRF = \frac{A_{NAT}}{A_{IS}} \times \frac{C_{IS}}{C_{NAT}} \qquad \text{(Equation 1.2)}$$

Where $A_{NAT}$ is the peak area for the "native" pollutants, $A_{IS}$ is the peak area of the internal standard, $C_{IS}$ is the concentration of the internal standard and $C_{NAT}$ is the concentration of the "native" compound in the standard. The relative standard deviation (RSD) of RRFs obtained for a given target compound should not exceed 10%. Table 2.6 shows RRF values obtained for each standard in a typical five point full calibration, as well as the average and relative standard deviation.

**Table 2.6: RRFs obtained for a typical five point calibration**

| Analyte | RRF-A | RRF-B | RRF-C | RRF-D | RRF-E | Average | %RSD |
|---|---|---|---|---|---|---|---|
| BDE-28 | 0.82 | 0.85 | 0.88 | 0.94 | 0.98 | 0.89 | 7.3 |
| PBEB | 0.89 | 0.82 | 0.90 | 0.83 | 0.88 | 0.86 | 4.2 |
| BDE-47 | 0.79 | 0.82 | 0.84 | 0.93 | 0.94 | 0.86 | 7.8 |
| BDE-100 | 0.84 | 0.84 | 0.89 | 0.92 | 0.91 | 0.88 | 4.3 |
| BDE-99 | 0.79 | 0.78 | 0.83 | 0.91 | 0.94 | 0.85 | 8.4 |
| EH-TBB | 6.19 | 6.56 | 6.13 | 6.24 | 6.46 | 6.32 | 2.9 |
| BDE-154 | 1.12 | 1.13 | 1.17 | 1.19 | 1.29 | 1.18 | 5.7 |
| BDE-153 | 1.29 | 1.28 | 1.37 | 1.36 | 1.46 | 1.35 | 5.4 |
| BDE-183 | 0.94 | 0.96 | 0.97 | 1.07 | 1.10 | 1.01 | 7.1 |
| BTBPE | 1.43 | 1.48 | 1.56 | 1.53 | 1.54 | 1.51 | 3.5 |
| BEH-TEBP | 1.02 | 1.17 | 1.10 | 1.18 | 1.11 | 1.12 | 5.8 |
| BDE-209 | 0.87 | 0.93 | 0.93 | 0.89 | 0.92 | 0.91 | 3.0 |
| DBDPE | 0.19 | 0.19 | 0.21 | 0.22 | 0.21 | 0.20 | 6.6 |

A single point continuing calibration (Std D) was analysed at the beginning and the end of each sample batch or at a minimum interval of 24 hours while sample analysis was being conducted. The RRFs obtained from this calibration standard must fall within 25% of the RRFs obtained for the initial 5- point calibration.

Chromatographic peaks were only accepted for quantification when they met the following criteria:

1. The signal to noise ratio of the peak for the least abundant ion monitored for that analyte exceeded 3:1.
2. The relative retention time (RRT) of the peak in the sample was within 0.2% of the average value determined for the calibration standards run before and after sample batch.
3. The ratio of the quantification and qualification ion of the peak in the sample was within 15% of the average value determined for the 2 calibration standards run before and after sample batch.

Figures 2.5 displays the elution order of PBDEs and NBFRs with IS and RDS in the calibration standard (Std D in the table 2.5). In addition, Figures 2.6 and 2.7 show chromatograms of a field blank and a UK indoor dust sample respectively.

**Figure 2.5: GC-MS chromatograms showing elution order of PBDE congeners, PCB-129 and NBFRs standards in calibration standard (Std D)**

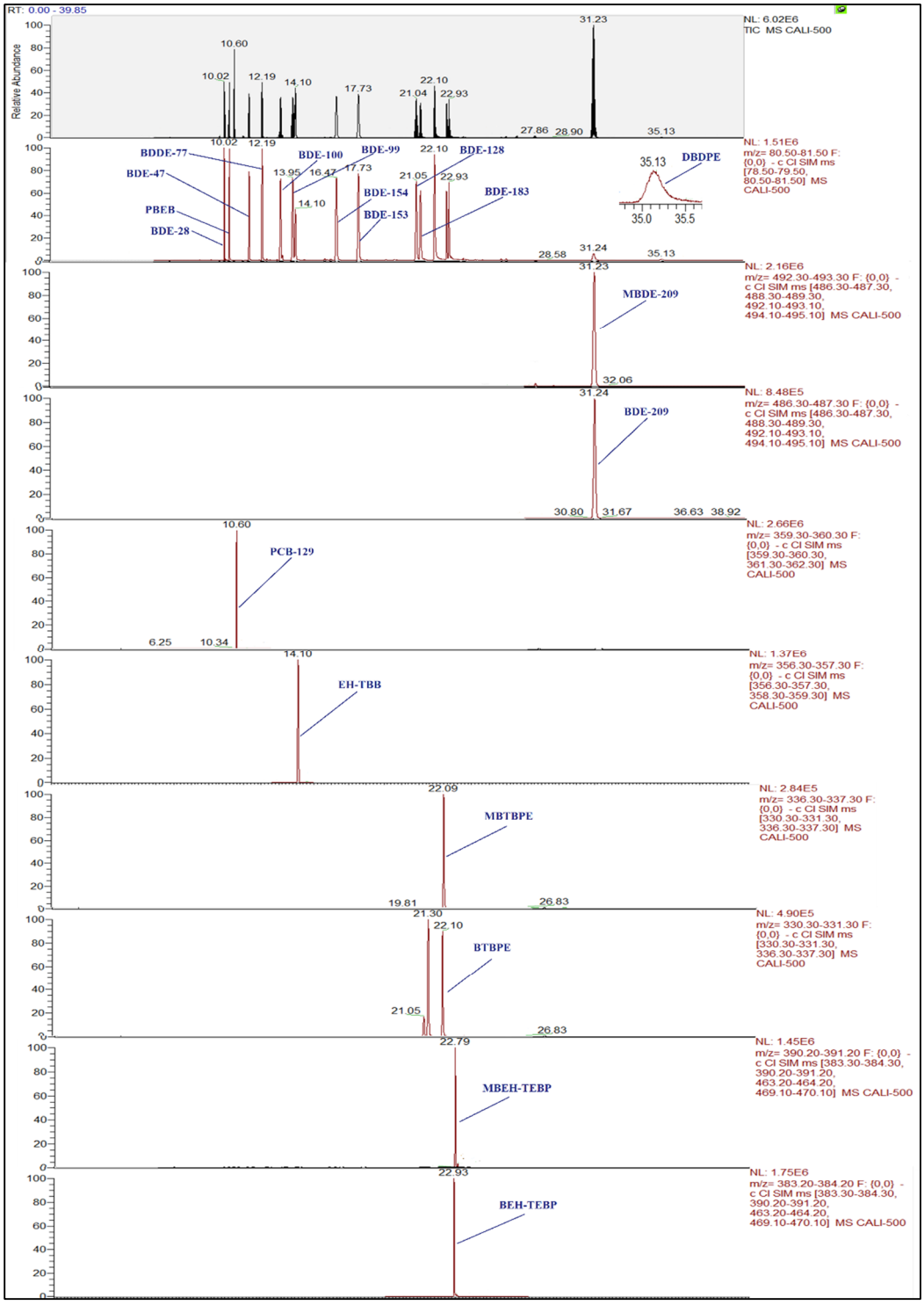


**Figure 2.6: GC-MS Chromatograms of a field blank**

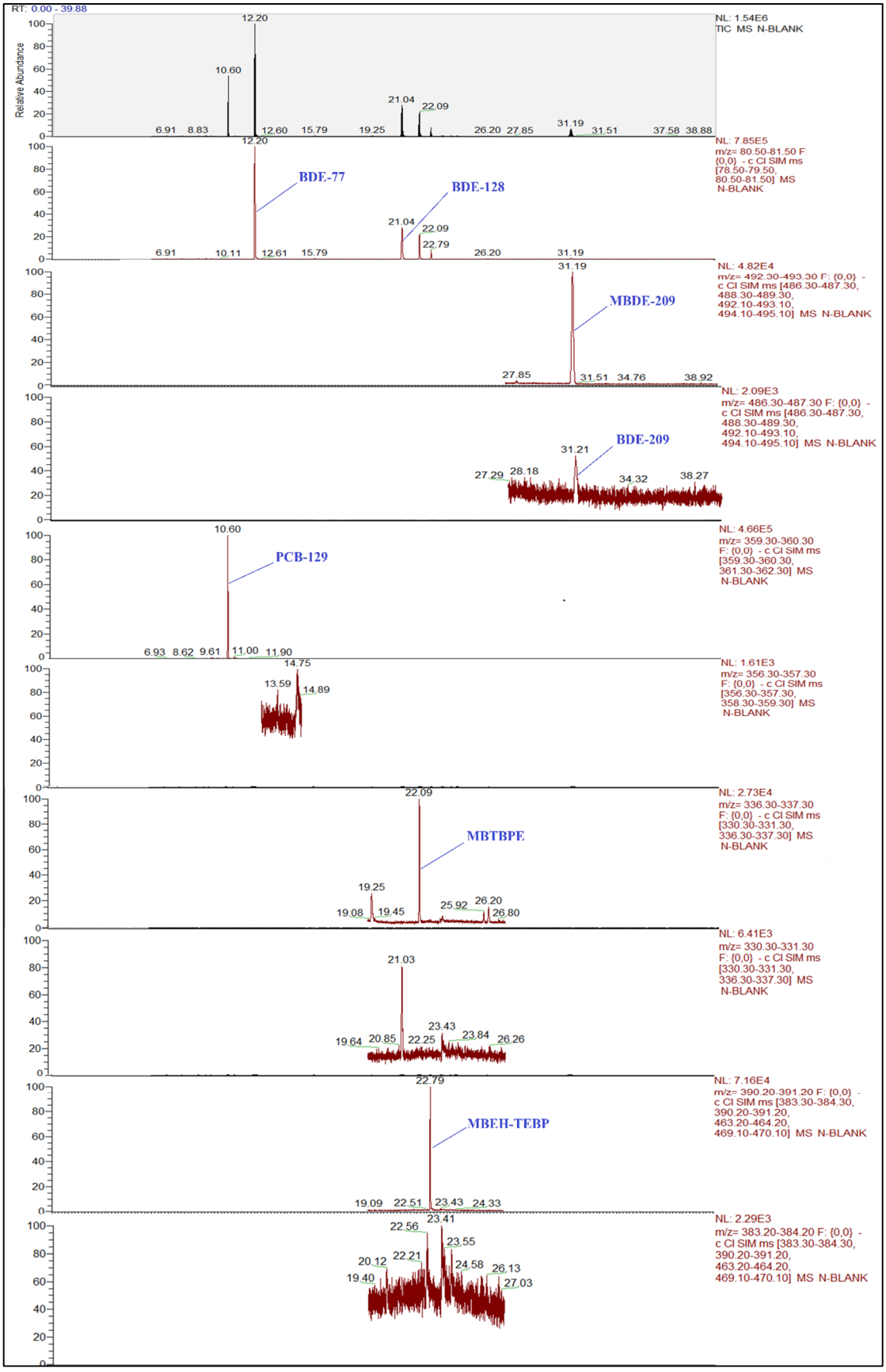
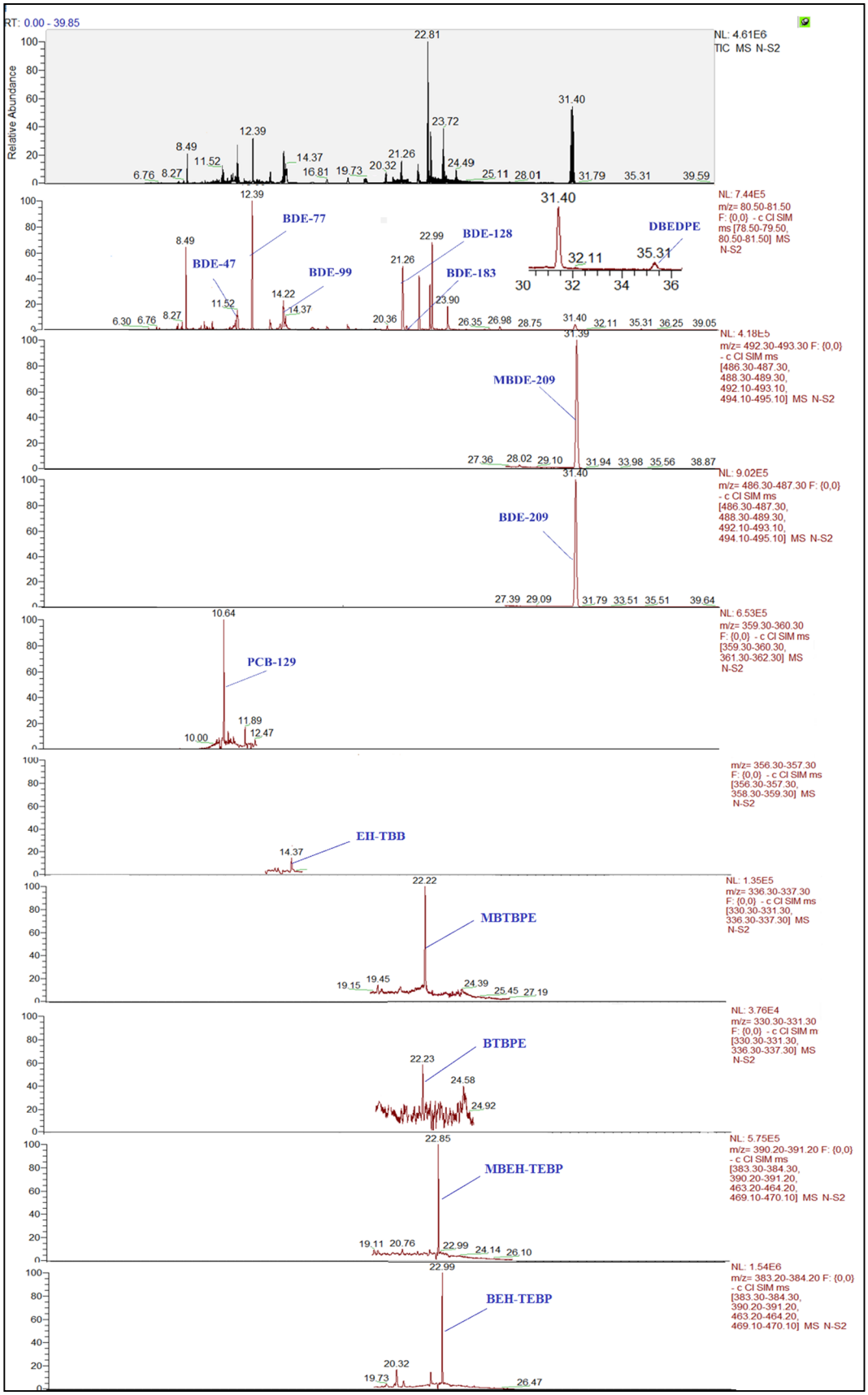


**Figure 2.7: GC-MS chromatograms showing UK indoor dust sample (H3R3ES)**



### 2.7.2 Determination of internal standard recoveries

Recoveries of internal standards (IS) were calculated by the addition of a recovery determination standard (RDS) to the final extract before injection on the GC/MS. These calculations were to assess the total loss of IS during extraction and clean-up method, assuming a zero loss of RDS (PCB-129) because it was added at the final stage. The recoveries of IS were calculated using equation 2.2

$$\% \text{ IS Recovery} = \left[\left(\frac{A_{IS}}{A_{RDS}}\right)_S \times \left(\frac{A_{RDS}}{A_{IS}}\right)_{STD} \times \left(\frac{C_{IS}}{C_{RDS}}\right)_{STD} \times \left(\frac{C_{RDS}}{C_{IS}}\right)_S\right] \times 100 \quad \text{(Equation 2.2)}$$

Where $(A_{IS}/A_{RDS})_S$ is the ratio of internal standard peak area to recovery determination standard peak area in the sample, $(A_{RDS}/A_{IS})_{STD}$ is the ratio of recovery determination standard peak area to internal standard peak area in the calibration standard, $(C_{IS}/C_{RDS})_{STD}$ is the ratio of concentration of internal standard to concentration of recovery determination standard in the calibration standard, and $(C_{RDS}/C_{IS})_S$ is the ratio of concentration of recovery determination standard to concentration of internal standard in the sample. The amount of RDS was 25 ng and amount of internal standards were as in table 2.3. Concentrations were not recovery corrected as the internal standard method inherently corrects for analyte losses. A statistical summary of the internal standard recoveries are listed in table 2.7.

**Table 2.7: Internal Standard recovery from dust samples analysed in this study (%)**

| Standard | Mean | Median | Minimum | Maximum | SD | %RSD |
|---|---|---|---|---|---|---|
| BDE-77 | 88 | 87 | 67 | 115 | 15 | 18 |
| BDE-128 | 90 | 87 | 65 | 110 | 12 | 13 |
| MBTBPE | 82 | 84 | 54 | 99 | 12 | 14 |
| MBEH-TEBP | 87 | 86 | 74 | 103 | 10 | 11 |
| MBDE-209 | 78 | 74 | 49 | 121 | 16 | 21 |

### 2.7.3 Evaluation of method accuracy and precision

The analytical method developed was validated using a standard reference material, SRM2585 from the US National Institute of Standards and Technology (NIST). This reference material has either certified or indicative concentrations for a range of compounds,

including our target PBDEs. Before commencing analysis of any dust samples, 6 replicate analyses of SRM2585 were conducted to obtain satisfactory results comparing with certified data. The mean concentrations and standard deviation values obtained for an initial set of six SRM2585 replicates with the certified values for selected PBDE congeners are provided in table 2.8.

**Table 2.8: Average concentrations (ng/g) ±standard deviation (STD) of PBDEs in SRM2585 (n=6) compared with certified values**

| Analyte | Concentration ± STD | Certified ± STD |
|---|---|---|
| BDE -28 | 49.2 ± 6.5 | 46.9±4.4 |
| BDE -47 | 491.4 ± 40.7 | 497±46 |
| BDE -99 | 887.6 ± 55.3 | 892±53 |
| BDE-100 | 151.2 ± 13 | 145±11 |
| BDE- 153 | 117.2 ± 10 | 119±1.0 |
| BDE- 154 | 86.6 ± 4.0 | 83.5±2.0 |
| BDE- 183 | 42.2± 4.6 | 43.5±3.5 |
| BDE- 209 | 2391.8 ± 219 | 2510±190 |

Due to the absence of certified or indicative values for NBFRs in SRM2585, the values obtained in this study were compared to available literature data reported by other reputable laboratories for this SRM. Table 2.9 lists NBFR values detected using our method for SRM2585. These appear in good agreement with the corresponding values reported in the literature.

**Table 2.9: Average (standard deviation) concentrations (ng/g) of NBFRs in SRM2585 (n=6) compared with average values reported in the literature**

| Analyte | This study | Stapleton et al., 2008 | Ali et al., 2011b | Van den Eede et al., 2012 | Sahlstrom et.al., 2012 | Cristale and Lacorte, 2013 |
|---|---|---|---|---|---|---|
| PBEB | 8.2 (1.3) | n.a | n.a | n.a. | n.a. | n.a. |
| EH-TBB | 35.5 (5.8) | <30 | 40 | 26 (2) | 36 (2.4) | 35 (6) |
| BTBPE | 58.3 (9.1) | <0.8 | 32 | 39 (14) | 39 (4.9) | 76 (4) |
| BEH-TEBP | 844 (58) | 145 (16.7) | 652 | 574 (49) | 1,300 | 857 (73) |
| DBDPE | <6 | <10 | <20 | <7.1 | <10 | n.a. |

Note: na = no data available

As an ongoing measure of accuracy, following the initial replicate analyses described above, an aliquot of SRM 2585 was analysed with every 20 dust samples. As a QA/QC check, concentration data obtained for these SRM aliquots had to fall within 30% of the average values obtained from the 6 initial replicate analyses (Table 2.8 and 2.9). Overall, fifteen replicates of SRM2585 were analysed with the data obtained proving satisfactory (RSD < 20%). Table 2.10 and 2.11 summarise PBDEs and NBFRs concentrations detected in SRM2585 in this study (ng/g)

**Table 2.10: PBDEs concentrations detected in SRM2585 (n=15) in this study (ng/g)**

| Parameter | BDE-28 | BDE-47 | BDE-99 | BDE-100 | BDE-153 | BDE-154 | BDE-183 | BDE-209 |
|---|---|---|---|---|---|---|---|---|
| Mean | 47.9 | 493.5 | 884.4 | 149.8 | 118.9 | 89.9 | 43.9 | 2386.7 |
| Median | 47.0 | 488.9 | 869.8 | 147.8 | 122.2 | 90.8 | 43.1 | 2291.7 |
| Min | 37.9 | 391.7 | 780.9 | 132.1 | 98.7 | 73.9 | 37.0 | 2028.7 |
| Max | 63.9 | 571.7 | 1030.3 | 169.5 | 130.9 | 101.3 | 56.4 | 2734.3 |
| SD | 6.9 | 41.9 | 98.5 | 12.3 | 10.4 | 7.9 | 6.3 | 224.5 |
| %RSD | 14.5 | 8.5 | 8.5 | 8.2 | 8.7 | 8.8 | 14.3 | 9.4 |

**Table 2.11: NBFRs concentrations detected in SRM2585 (n=15) in this study (ng/g)**

| Parameter | PBEB | EH-TBB | BTBPE | BEH-TEBP | *DBDPE |
|---|---|---|---|---|---|
| Mean | 8.7 | 35.7 | 53.9 | 831.9 | - |
| Median | 8.6 | 34.6 | 53.3 | 802.0 | - |
| Min | 6.6 | 25.8 | 36.3 | 658.0 | - |
| Max | 11.2 | 43.3 | 69.3 | 1061.5 | - |
| SD | 1.2 | 5.2 | 7.5 | 117.6 | - |
| %RSD | 13.9 | 15.2 | 14.0 | 14.1 | - |

* DBDPE was not detected (< 6 ng/g) in all SRM2585 samples.

### 2.7.4 Method blanks and field blanks

Method blanks (n = 60) were conducted to evaluate the extent of any contamination with target compounds as a result of the extraction and clean-up. In such blanks, the dust sample is omitted and replaced with 0.1 g of hexane washed anhydrous sodium sulfate. One such method blank was processed with each batch of five dust samples. Field blanks (n = 14) were also conducted to assess any contamination contributed as a result of sampling, transport and storage of samples, in addition to any introduced as a result of extraction and clean-up. The tri to hepta PBDEs, PBEB, EH-TBB, BTBPE and DBDPE were not detected in any of these blank samples. Very low concentrations of BEH-TEBP and BDE-209 were detected in comparable levels in both method and field blanks. The mean concentrations were 1.72 and 2.52 ng/g with standard deviation 0.51 and 0.69 for BEH-TEBP and BDE-209 respectively.

### 2.7.5 Determination of detection limits

The instrumental detection limit (IDL) or limit of detection (LOD) is defined as the lowest mass of an analyte that gives a signal to noise ratio of 3:1 on the instrument. The limit of quantification (LOQ) is defined as the lowest amount of an analyte that can be quantitatively determined with acceptable precision and accuracy, which was calculated as the mass generating a 10:1 signal to noise ratio. Where a target compound (as was the case in some instances for BEH-TEBP and BDE-209) was detected in a blank, the LOQ for that analyte was calculated as the mean plus 3 times the standard deviation of the concentrations detected in 10 blank samples. This is called the Minimum Reported Value (MRV). The values of LOD, LOQ and MRV are listed in table 2.12.

**Table 2.12: Limit of detection (LOD), Limit of quantification (LOQ) and Minimum Reported Value (MRV) values (pg/ injection) for PBDEs and NBFRs in this study**

| Analyte | LOD | LOQ | MRV |
|---|---|---|---|
| BDE-28 | 0.09 | 0.29 | - |
| BDE-47 | 0.11 | 0.36 | - |
| BDE-100 | 0.14 | 0.46 | - |
| BDE-99 | 0.16 | 0.54 | - |
| BDE-154 | 0.22 | 0.72 | - |
| BDE-153 | 0.24 | 0.79 | - |
| BDE-183 | 0.2 | 0.66 | - |
| BDE-209 | 0.25 | 0.84 | 4.59 |
| PBEB | 0.08 | 0.27 | - |
| EH-TBB | 0.51 | 1.71 | - |
| BTBPE | 2.83 | 9.43 | - |
| BEH-TEBP | 0.48 | 1.61 | 3.26 |
| DBDPE | 6.02 | 20.08 | - |

### 2.7.6 Calculation of concentrations in samples

The average of RRFs obtained using equation 1 in 2.7.1 for two or more calibration standards were used to calculate the concentration of the analytes (ng/g) in dust samples according to equation 2.3

$$\text{Concentration} = \frac{A_{NAT}}{A_{IS}} \times \frac{1}{\text{RRF}} \times \frac{M_{IS}}{SS} \quad \text{(Equation 2.3)}$$

Where $A_{NAT}$ is the peak area of the target compound in the sample, $A_{IS}$ is the peak area of the internal standard in the sample, RRF is the relative response factor for the target pollutant, $M_{IS}$ is the mass of internal standard added to the sample (pg) and SS is the sample size (g). This equation was applied directly using XCALIBUR software 2.2 SP1.

## 2.8 Determination of organic carbon content in dust samples

The total organic carbon content (TOC) of dust samples was obtained using a Total Organic Carbon analyser TOC-$V_{CSH/CSN}$ combined with Solid Sample Module SSM-5000 (both SHIMADZU, Japan). The analytical method covers the determination of Total Carbon (TC) and Inorganic Carbon (IC), hence the TOC was deduced by subtracting the IC from the TC value. Prior to starting analysis, all dust samples were dried at 105 ˚C for 24 hours. For TC determination, an aliquot of dust (typically 10-15 mg) in a small ceramic boat was put into the TC furnace at 900 ˚C and burned in pure oxygen, with the released carbon dioxide measured in the TOC detector. For IC determination, an aliquot of the same homogenised dust sample in a ceramic boat was covered with a sufficient amount of 25% phosphoric acid, burned in the IC furnace at 200˚C, and the released carbon dioxide measured using the same TOC detector.

To discriminate and quantify carbon dioxide, sucrose (TC content 40%) and sodium bicarbonate (IC content 14.3%) were used as standard substances for total carbon and inorganic carbon calibration of the Shimadzu TOC- $V_{CSH/CSN}$ analyzer respectively. The calibration range was 5 mg, 10 mg, 15 mg, 20 mg, and 25 mg for both sucrose and sodium bicarbonate. Linear calibration plots were obtained for both standards ($R^2 > 0.999$).

## 2.9 Statistical analysis

Statistical analysis of the data was performed using Microsoft Excel 2013 and IBM SPSS statistics software (V. 20). Mean, median, maximum and minimum were considered to evaluate quantitative levels and pattern distribution of PBDEs and NBFRs in dust samples. In addition, median concentrations were preferred for direct comparison. The distribution of the concentration data for target pollutants was tested using the Shapiro-Wilk test. Due to the fact that the data were highly skewed, all data were log-transformed prior to comparison of means via T-test analysis and One-way Repeated Measures (ANOVA) for testing significant differences between arithmetic means. All concentrations below LOQ were assigned a value of 0.5 LOQ/ MRV. Potential correlations between various parameters were investigated using Pearson Correlation. A p value < 0.05 was used as the level indicating statistical significance.

# CHAPTER 3

# WITHIN-ROOM AND WITHIN-HOME SPATIAL VARIABILITY IN CONCENTRATIONS OF PBDEs AND NBFRs IN INDOOR DUST

## 3.1 Summary

To test the hypothesis that human exposure assessments of PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209) and NBFRs (PBEB, EH-TBB, BEH-TEBP, BTBPE and DBDPE) via dust ingestion are affected by spatial variability, dust samples were collected from three different rooms (living room, bedroom and study) in three homes in Birmingham UK. In each room, three different dust samples were taken at monthly intervals for nine months, one sample from elevated surfaces and two samples from two different floor areas. As indicated by their detection frequency, the main BFRs taken into account for statistical analysis are $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs. Within-room spatial variability in concentrations of PBDEs and NBFRs was evaluated using a paired t-test applied to samples: a) taken from two different floor areas; and b) taken from elevated surface and floor dust. Within- home spatial variability was tested on samples taken from different rooms in the same home via a repeated measures ANOVA test.

In the nine investigated rooms, our findings related to within-room spatial variability are that: no significant differences in BFR concentrations exist between different floor areas in the same room, except for $\Sigma_7$tri-hepta-BDEs in two bedrooms and one study, BEH-TEBP in one bedroom, DBDPE in one bedroom and one study, and $\Sigma_5$NBFRs in one bedroom, one study room and one living room. When data for all nine studied rooms were considered together, concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and $\Sigma_5$NBFRs in elevated surface dust exceeded significantly those in floor dust, while in contrast, concentrations of DBDPE in floor dust exceeded significantly those in dust from elevated surfaces. When data were considered on an individual room basis, concentrations of $\Sigma_7$tri-hepta-BDEs, BEH-TEBP, BDE-209, DBDPE, and $\Sigma_5$NBFRs in elevated surface dust differed significantly from those in matched floor dust samples in 7, 5, 4, 4 and 4 rooms respectively. Substantial within- room variation in concentrations of BFRs in floor dust was detected and attributable to varying distances from potential BFR sources.

Our within-home (or between-room) spatial variability data reveal some significant differences in concentrations of our target contaminants. In Home 1, concentrations of BDE-209 in bedroom dust exceeded significantly those in living room dust. In Home 2, concentrations of $\Sigma_7$tri-hepta-BDEs in the study exceeded significantly those in the living room. In contrast, BDE-209 concentrations in the living room exceeded significantly those in the study, while those of BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in the study exceeded significantly those in the bedroom. In Home 3, concentrations of BEH-TEBP and $\Sigma_5$NBFRs decreased significantly between rooms in the order: child's bedroom > adult bedroom > living room. These differences are likely attributable to differences between the contents of the rooms studied.

Based on our findings, for human exposure assessments, we recommended sampling more than one floor dust sample depending on the dimensions of the room, and all elevated surfaces with which with the occupants have contact.

## 3.2 Sampling protocol and locations

From each of three homes (H1, H2, and H3) in Birmingham, UK, 238 indoor dust samples were collected at monthly intervals from three different rooms (R1 = living room, R2 = adult bedroom, and R3 = study or child's bedroom in H3). In the three homes, living rooms were located on the ground floor with bedrooms were located on the first floor. In Home 1 and 2, the studies were located on the ground floor. In each of the nine investigated rooms, two dust samples were obtained from two different floor areas F1 and F2, following the sampling protocol described in chapter 2, with an additional dust sample collected from the elevated surfaces (ES), such as sofas, tables, shelves, and large articles present on tables and shelves. Dust was not collected from under furniture or from highly elevated surfaces with which human contact is rare, such as the tops of wardrobes. Sampling was conducted for nine months between May 2013 and March 2014, with the exception of July and August 2013 (Iraqi dust samples were collected at that time). Because of the low dust loading on elevated surfaces, 2-3 dust samples from elevated surfaces were combined into one sample for analysis.

In addition to the data recorded in the questionnaire (Appendix 1), nine models of each room were designed according to the room contents via a home designer website (floor planner.com), along with the sampling locations that refer to the floor dust sample areas (F1

and F2) and elevated surface dust sample locations (ES). Figures 3.1, 3.2, and 3.3 illustrate the room contents of Home 1, Home 2 and Home 3 respectively. These models represent room contents *in situ* in the first month of the sampling campaign. Details of any changes in room contents are described in section 4.3.3, Chapter 4 which addresses within-room and within-home temporal variation in BFR concentrations in house dust.

**Figure 3.1: Room contents and sampling locations relative to floor (F1 and F2) and elevated surface (ES) dust sampling locations in the living room (H1R1), bedroom (H1R2) and study room (H1R3) of Home 1**

**Figure 3.2: Room contents and sampling locations relative to floor (F1 and F2) and elevated surface (ES) dust sampling locations in the living room (H2R1), bedroom (H2R2) and study room (H2R3) of Home 2**

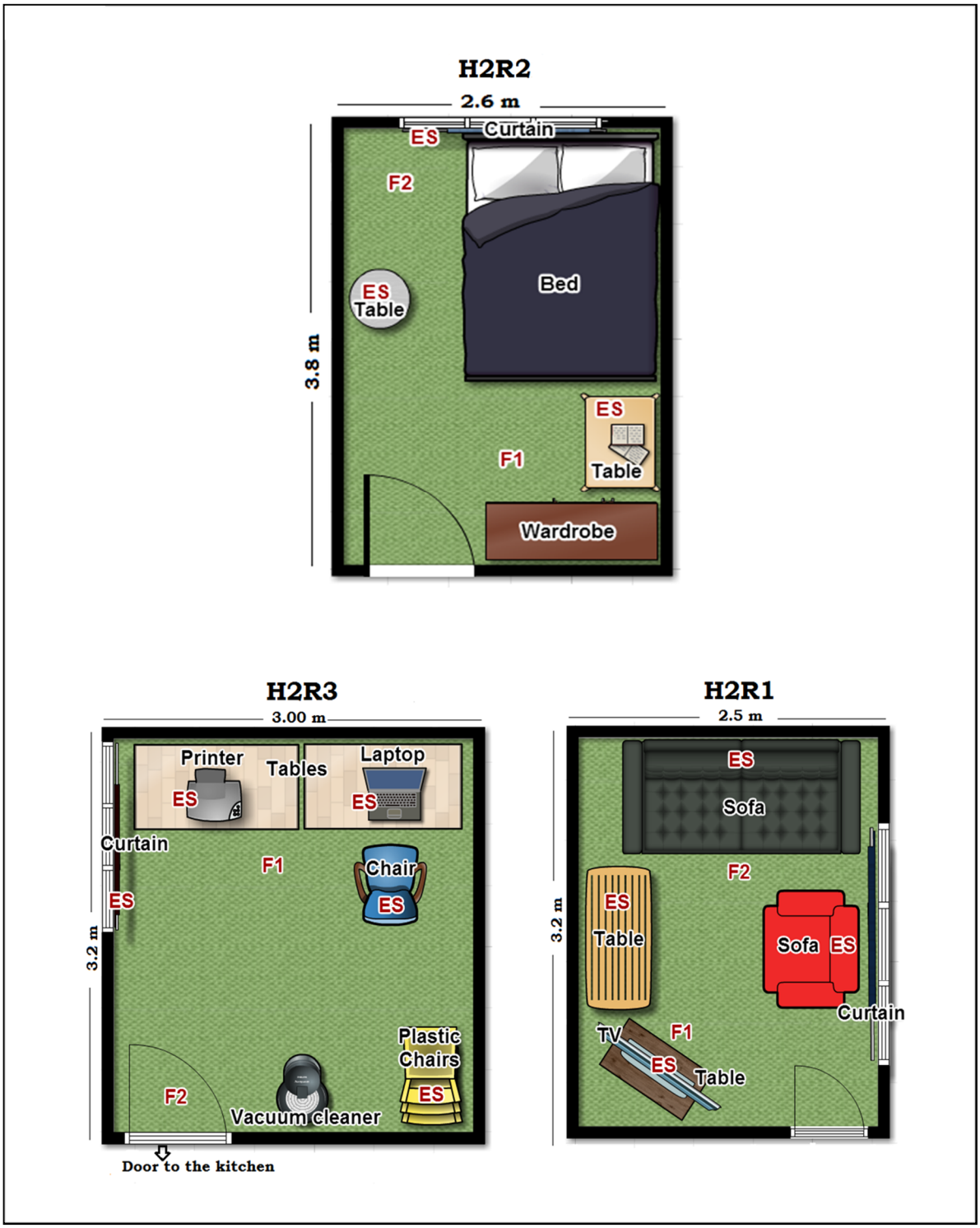


**Figure 3.3: Room contents and sampling locations relative to floor (F1 and F2) and elevated surface (ES) dust sampling locations in the living room (H3R1), adult bedroom (H3R2) and a child's bedroom (H3R3) of Home 3**

## 3.3 Results and discussion

### 3.3.1 Detection frequency and relationship between BFRs in indoor dust samples

In the three investigated homes, the detection frequency of PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209) and NBFRs (PBEB, EH-TBB, BTBPE, BEH-TEBP, and DBDPE) ranged from 0% to 100%. The detection frequencies of BDE-209 and BEH-TEBP were 100%, followed by DBDPE with 100%, 97% and 94% in Home 1, Home 2 and Home 3 respectively. The highest detection frequency of BDE-47, BDE-99 and BDE-183 were found in Home 2 with 91%, 100% and 97% respectively. The highest detection frequency of EH-TBB was found in Home 3 with 96%, while that of BTBPE was found in Home 1 with 90%. The detection frequencies of BDE-28, BDE-100, BDE-153, BDE-154, and PBEB were < 90%. Table 3.1 shows the detection frequency of PBDEs and NBFRs in H1, H2 and H3.

**Table 3.1: Detection frequency of PBDEs and NBFRs in dust sample Home 1, Home 2 and Home 3**

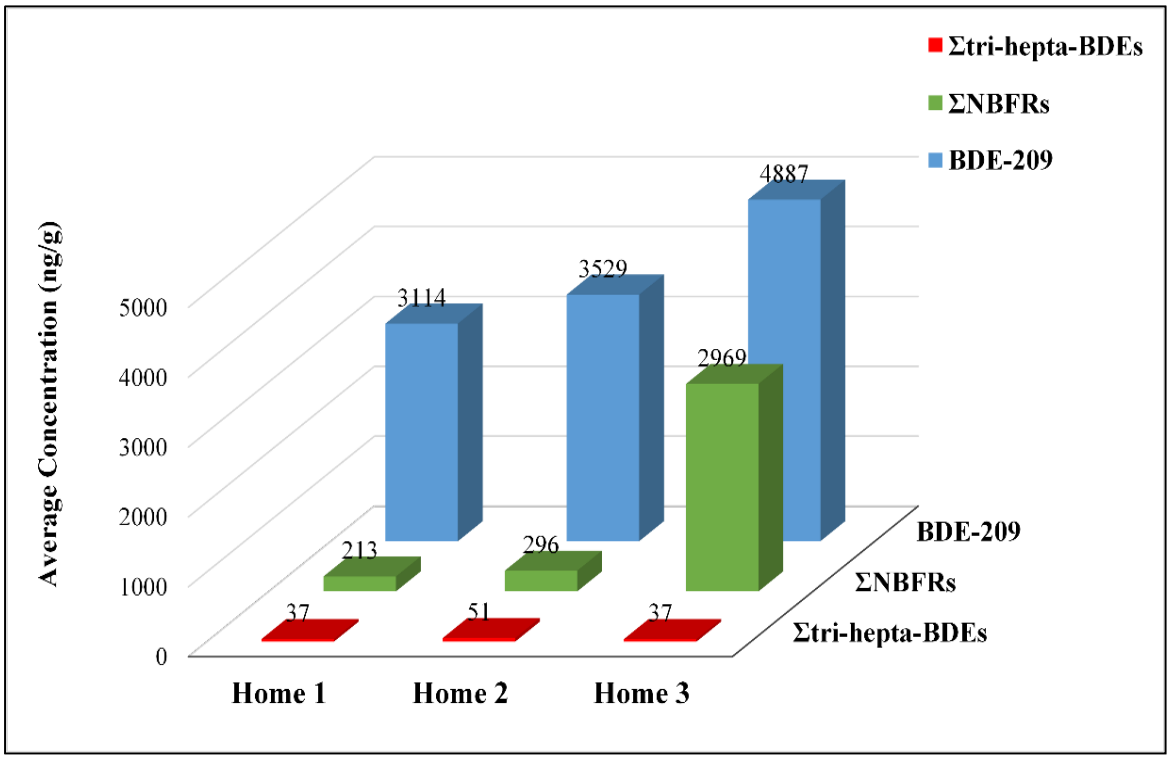
| Analyte | Home 1 (n= 61) | Home 2 (n= 66) | Home 3 (n= 66) |
|---|---|---|---|
| BDE-28 | 54 | 58 | 44 |
| BDE-47 | 80 | 91 | 56 |
| BDE-100 | 62 | 68 | 15 |
| BDE-99 | 93 | 100 | 86 |
| BDE-154 | 64 | 64 | 23 |
| BDE-153 | 89 | 76 | 88 |
| BDE-183 | 72 | 97 | 79 |
| BDE-209 | 100 | 100 | 100 |
| PBEB | 56 | 0 | 0 |
| EH-TBB | 59 | 47 | 96 |
| BTBPE | 90 | 85 | 82 |
| BEH-TEBP | 100 | 100 | 100 |
| DBDPE | 100 | 97 | 94 |

In addition to the low detection frequencies of BDE-28, BDE-100, BDE-153, and BDE-154, concentrations of these compounds were generally very low, and they were thus excluded from statistical analysis for individual comparison and not presented in summary

concentration tables. However, they were included in calculation of $\Sigma_7$tri-hepta-BDEs which refers to the sum of seven congeners (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, and BDE-183), $\Sigma_5$NBFRs represents the sum of five NBFRs (PBEB, EH-TBB, BTBPE, BEH-TEBP, and DBDPE), with ΣBFRs equalling the sum of $\Sigma_7$tri-hepta-BDEs, BDE-209 and $\Sigma_5$NBFRs.

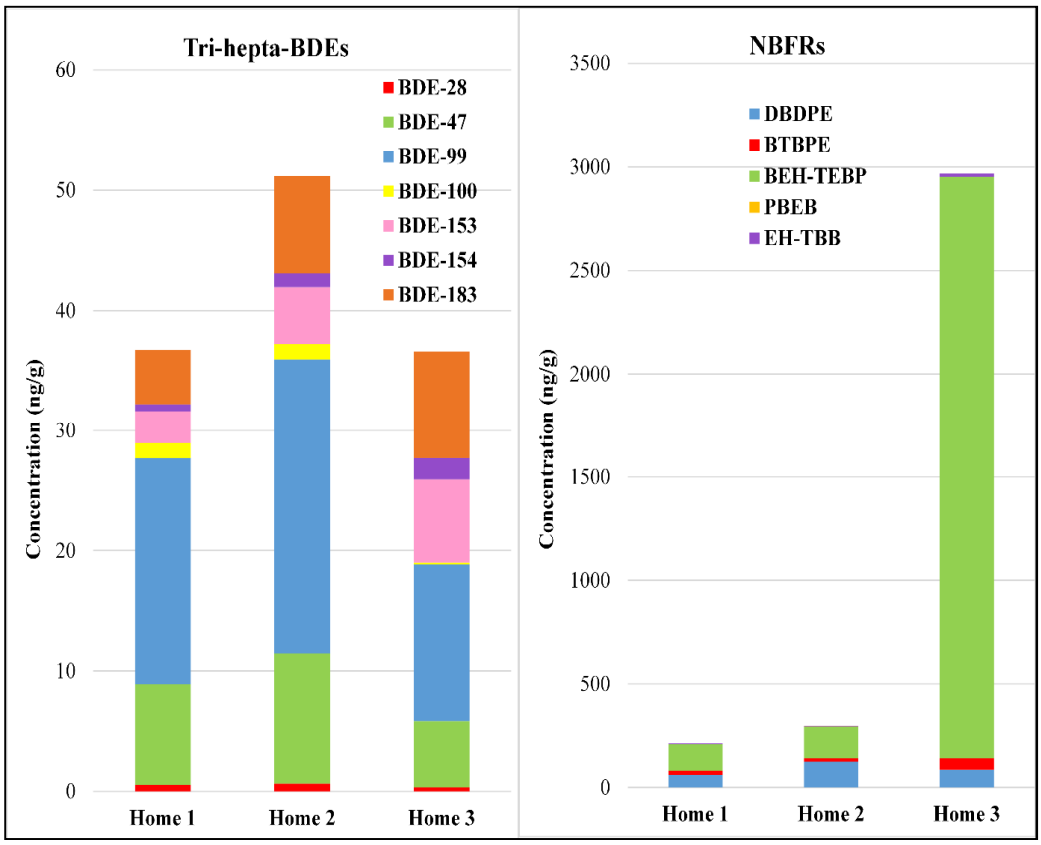
Among all target BFRs, BDE-209 was predominant, making average percentage contributions to ΣBFRs of 92.3%, 90.9%, and 62.8% in H1, H2 and H3 respectively. The high relative abundance of BDE-209 are not surprising, as Deca-BDE is the main BFR used in the UK (Harrad et al., 2008a: 2008b). The next most abundant was $\Sigma_5$NBFRs making average percentage contributions of 6.6%, 7.8% and 36.7% in H1, H2 and H3 respectively. $\Sigma_7$tri-hepta-BDEs made the lowest average percentage contributions of our target BFRs; specifically 1.1%, 1.3% and 0.5% of ΣBFRs in H1, H2 and H3 respectively. Figure 3.4 illustrates average concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209 and $\Sigma_5$NBFRs in H1, H2 and H3.

**Figure 3.4: Average concentrations (ng/g) of $\Sigma_7$tri-hepta-BDEs, BDE-209 and $\Sigma_5$NBFRs in Home 1, Home 2 and Home 3**



Of our target NBFRs, BEH-TEBP predominated making corresponding mean percentage contributions to $\Sigma_5$NBFRs of 59.8%, 52.4% and 94.7%, followed by DBDPE which made percentage contributions of 28.3%, 41.7% and 2.9% in H1, H2 and H3 respectively. The summation of EH-TBB, BTBPE and PBEB were the least abundant of the target NBFRs contributing 11.9%, 5.9% and 2.4% of $\Sigma_5$NBFRs in H1, H2 and H3 respectively. Of our target tri-hepta-BDEs, BDE-99, BDE-47 and BDE-183 were the highest percentage contributors to $\Sigma_7$tri-hepta-BDEs. Figure 3.5 shows average concentrations and distribution profiles of tri-hepta-BDEs and NBFRs in Home 1, Home 2 and Home 3.

**Figure 3.5: Average concentrations (ng/g) and distribution profiles of tri-hepta-BDEs and NBRs in Home 1, Home 2 and Home 3**




### 3.3.2 Concentrations of PBDEs and NBFRs in indoor dust samples

In the three investigated homes, only those BFRs displaying detection frequencies ≥ 90% were taken into account for statistical summary. In Home 1, concentrations of BDE-99, $\Sigma_7$tri-hepta-BDEs and DBDPE ranged between < dl- 101, < dl- 186 and 7.7- 243 ng/g respectively,

with the highest concentrations found in elevated surface dust of the bedroom (H1R2). Concentrations of BDE-209 and BTBPE ranged between 967-8319 and < dl-109 ng/g respectively, with the highest concentrations found in elevated surface dust in the study (H1R3). BEH-TEBP levels ranged between 47 and 674 ng/g with the highest concentration found in an elevated surface dust sample from the living room (H1R1). Finally, concentrations of $\Sigma_5$NBFRs ranged between 91 and 936 ng/g with the highest concentration found in a living room elevated surface dust sample. Tables 3.2, 3.3 and 3.4 provide a statistical summary of concentrations of BDE-99, $\Sigma_7$tri-hepta-BDEs, BDE-209, BTBPE, BEH-TEBP DBDPE and $\Sigma_5$NBFRs in dust samples from two floor areas (F1 and F2) and elevated surfaces (ES) in the living room (H1R1), bedroom (H1R2), and study room (H1R3) of Home 1 respectively.

**Table 3.2: Concentrations (ng/g) of BDE-99, $\Sigma_7$tri-hepta-BDEs, BDE-209, BTBPE, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in indoor dust from two floor areas (F1 and F2) and elevated surface (ES) dust samples in the living room of Home 1 (H1R1)**

| Sampling area | Parameter | BDE-99 | $\Sigma_7$tri-hepta-BDEs | BDE-209 | BTBPE | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|---|---|---|
| **F1** | Average | 9.7 | 21.1 | 2061 | 13.5 | 92.5 | 39.5 | 151 |
| | SD | 2.9 | 9.2 | 593 | 6.4 | 21.6 | 25.2 | 34 |
| | Minimum | 6.0 | 9.7 | 1425 | 6.1 | 64.8 | 13.9 | 102 |
| | Maximum | 14.0 | 38.6 | 3240 | 26.7 | 137.6 | 89.3 | 196 |
| **F2** | Average | 9.6 | 18.4 | 1901 | 8.4 | 85.2 | 42.0 | 142 |
| | SD | 3.6 | 6.4 | 859 | 6.7 | 13.8 | 25.2 | 38 |
| | Minimum | 3.9 | 11.2 | 970 | 2.4 | 60.3 | 15.6 | 91 |
| | Maximum | 14.2 | 29.9 | 3433 | 23.3 | 111.9 | 73.6 | 189 |
| **ES** | Average | 23.8 | 69.7 | 3679 | 71.6 | 323.3 | 131.2 | 540 |
| | SD | 8.1 | 19.3 | 827 | 18.6 | 236.6 | 47.0 | 268 |
| | Minimum | 16.3 | 43.7 | 2475 | 45.3 | 177.7 | 83.1 | 342 |
| | Maximum | 34.9 | 90.2 | 4334 | 89.1 | 673.8 | 178.2 | 936 |

**Table 3.3: Concentrations (ng/g) of BDE-99, $\Sigma_7$tri-hepta-BDEs, BDE-209, BTBPE, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in indoor dust from two floor areas (F1 and F2) and elevated surface (ES) dust samples in the bedroom of Home 1(H1R2)**

| Sampling area | Parameter | BDE-99 | $\Sigma_7$tri-hepta-BDEs | BDE-209 | BTBPE | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|---|---|---|
| **F1** | Average | 13.1 | 23.4 | 3342 | 12.3 | 127.1 | 71.2 | 216 |
| | SD | 11.4 | 21.6 | 1699 | 12.8 | 16.5 | 57.1 | 76 |
| | Minimum | < 0.16 | < 0.24 | 1008 | > 2.8 | 101.1 | 24.2 | 146 |
| | Maximum | 27.9 | 53.0 | 7064 | 41.2 | 158.0 | 196.0 | 367 |
| **F2** | Average | 19.0 | 33.6 | 2786 | 8.9 | 105.7 | 41.3 | 159 |
| | SD | 15.5 | 28.9 | 665 | 8.2 | 19.6 | 20.8 | 43 |
| | Minimum | < 0.16 | 3.5 | 1628 | > 2.8 | 72.8 | 18.2 | 109 |
| | Maximum | 41.6 | 83.7 | 3813 | 22.2 | 141.3 | 86.2 | 227 |
| **ES** | Average | 70.9 | 127.9 | 6506 | 7.9 | 168.4 | 90.4 | 268 |
| | SD | 20.9 | 39.5 | 1626 | 2.4 | 44.9 | 105.6 | 132 |
| | Minimum | 54.1 | 102.8 | 4244 | 5.7 | 115.2 | 7.7 | 129 |
| | Maximum | 101.3 | 186.3 | 7902 | 11.2 | 223.3 | 243.2 | 432 |

**Table 3.4: Concentrations (ng/g) of BDE-99, $\Sigma_7$tri-hepta-BDEs, BDE-209, BTBPE, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in indoor dust from two floor areas (F1 and F2) and elevated surface (ES) dust samples in the study of Home 1 (H1R3)**

| Sampling area | Parameter | BDE-99 | $\Sigma_7$tri-hepta-BDEs | BDE-209 | BTBPE | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|---|---|---|
| **F1** | Average | 10.9 | 21.7 | 2334 | 26.3 | 110 | 70 | 207 |
| | SD | 11.8 | 26.7 | 689 | 22.6 | 39 | 56 | 83 |
| | Minimum | 2.2 | 4.2 | 30 | 7.3 | 35 | 20 | 40 |
| | Maximum | 40 | 88.2 | 3366 | 72.3 | 153 | 194 | 358 |
| **F2** | Average | 9.7 | 17.2 | 2777 | 15.3 | 66.1 | 29.4 | 113 |
| | SD | 3.1 | 8.7 | 339 | 7.4 | 18.9 | 18.4 | 15 |
| | Minimum | 6.7 | 9.3 | 2303 | 7.9 | 46.7 | 16.2 | 92 |
| | Maximum | 12.8 | 26.9 | 3077 | 22.6 | 85.1 | 56.5 | 125 |
| **ES** | Average | 41.4 | 79.1 | 6572 | 54.6 | 225.4 | 78.0 | 365 |
| | SD | 19.5 | 37.7 | 2767 | 36.4 | 30.1 | 47.9 | 61 |
| | Minimum | 17.2 | 28.7 | 2456 | 31.9 | 188.5 | 41.5 | 329 |
| | Maximum | 62.4 | 119.6 | 8319 | 108.8 | 257.1 | 146.2 | 455 |

In Home 2, BDE-47 concentrations ranged from < dl to 45 ng/g, with the highest concentration found in an elevated surface dust sample from the bedroom (H2R2). Concentrations of BDE-99, $\Sigma_7$tri-hepta-BDEs and DBDPE ranged between 0.47- 68, 3.6-180 and < dl-433 ng/g respectively, with the highest concentration found in the study (H2R3) for BDE-99, $\Sigma_7$tri-hepta-BDEs in elevated surface dust, and for DBDPE in floor dust. Concentrations of BDE-183, BDE-209 and BEH-TEBP ranged between < dl- 42, 1,650-11,105 and 18- 722 ng/g, with maximum concentrations of each found in living room elevated surface dust. Tables 3.5, 3.6 and 3.7 provide a statistical summary of concentrations of BDE-47, BDE-99, BDE-183, $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and $\Sigma_5$NBFRs in dust samples from two floor areas (F1 and F2) and elevated surfaces (ES) from the living room, bedroom and study of Home 2 respectively

**Table 3.5: Concentrations (ng/g) of BDE-47, BDE-99, BDE-183, $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in indoor dust from two floor areas (F1 and F2) and elevated surface (ES) dust samples in the living room of Home 2 (H2R1)**

| Sampling area | Parameter | BDE-47 | BDE-99 | BDE-183 | $\Sigma_7$tri-hepta-BDEs | BDE-209 | BEH-TEBP | DBDPE | Σ5NBFRs |
|---|---|---|---|---|---|---|---|---|---|
| F1 | Average | 5.1 | 13.3 | 7.1 | 30.9 | 3414 | 120.0 | 129.8 | 263 |
| | SD | 2.6 | 7.0 | 4.4 | 11.1 | 915 | 25.0 | 93.9 | 109 |
| | Minimum | < 0.1 | 3.1 | 2.6 | 12.6 | 2264 | 92.2 | 38.0 | 153 |
| | Maximum | 7.7 | 21.6 | 15.3 | 42.1 | 5034 | 165.1 | 304.3 | 442 |
| F2 | Average | 4.3 | 12.6 | 7.3 | 29.5 | 3123 | 105.0 | 101.9 | 217 |
| | SD | 3.1 | 5.1 | 6.4 | 9.3 | 889 | 42.5 | 79.8 | 116 |
| | Minimum | < 0.1 | 4.8 | 2.0 | 15.6 | 1650 | 18.3 | 9.4 | 42 |
| | Maximum | 9.4 | 20.7 | 21.7 | 42.6 | 4344 | 167.4 | 261.7 | 440 |
| ES | Average | 19.8 | 43.5 | 35.1 | 110.7 | 7269 | 445.2 | 56.2 | 523 |
| | SD | 7.9 | 14.2 | 7.3 | 28.8 | 2908 | 289.6 | 34.9 | 312 |
| | Minimum | 11.1 | 26.9 | 26.4 | 79.7 | 4355 | 87.3 | 19.6 | 131 |
| | Maximum | 29.6 | 59.6 | 41.7 | 148.6 | 11105 | 722.4 | 98.3 | 839 |

**Table 3.6: Concentrations (ng/g) of BDE-47, BDE-99, BDE-183, $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in indoor dust from two floor areas (F1 and F2) and elevated surface (ES) dust samples in the bedroom of Home 2 (H2R2)**

| Sampling area | Parameter | BDE-47 | BDE-99 | BDE-183 | $\Sigma_7$tri-hepta-BDEs | BDE-209 | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|---|---|---|---|
| **F1** | Average | 5.5 | 13.4 | 3.8 | 27.0 | 2687 | 112.7 | 92.1 | 231 |
| | SD | 3.7 | 11.4 | 2.7 | 17.2 | 451 | 29.9 | 51.3 | 74 |
| | Minimum | < 0.1 | 0.5 | < 0.2 | 3.6 | 1907 | 83.8 | 31.3 | 135 |
| | Maximum | 11.0 | 33.7 | 8.7 | 53.9 | 3301 | 182.7 | 193.9 | 339 |
| **F2** | Average | 18.8 | 32.2 | 4.3 | 62.1 | 2947 | 111.1 | 117.1 | 247 |
| | SD | 6.5 | 10.2 | 1.2 | 17.1 | 710 | 60.6 | 67.2 | 118 |
| | Minimum | 11.4 | 16.0 | 2.4 | 31.5 | 1955 | 71.6 | 31.2 | 103 |
| | Maximum | 30.6 | 44.8 | 6.1 | 81.8 | 3796 | 267.5 | 226.3 | 465 |
| **ES** | Average | 28.0 | 44.4 | 5.5 | 82.7 | 6675 | 135.3 | 26.7 | 186 |
| | SD | 11.4 | 13.3 | 3.6 | 28.7 | 2722 | 42.9 | 25.5 | 68 |
| | Minimum | 17.6 | 26.2 | < 0.2 | 51.0 | 3511 | 95.1 | 9.6 | 115 |
| | Maximum | 44.6 | 58.6 | 8.3 | 120.9 | 10168 | 197.0 | 66.2 | 279 |

**Table 3.7: Concentrations (ng/g) of BDE-47, BDE-99, BDE-183, $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in indoor dust from two floor areas (F1 and F2) and elevated surface (ES) dust samples in the study of Home 2 (H2R3)**

| Sampling area | Parameter | BDE-47 | BDE-99 | BDE-183 | $\Sigma_7$tri-hepta-BDEs | BDE-209 | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|---|---|---|---|
| **F1** | Average | 9.9 | 24.9 | 5.0 | 48.0 | 2672 | 119.8 | 133.6 | 265 |
| | SD | 4.5 | 7.7 | 1.1 | 14.1 | 521 | 18.2 | 66.9 | 70 |
| | Minimum | 4.6 | 11.9 | 3.2 | 28.1 | 1789 | 90.9 | 60.2 | 197 |
| | Maximum | 20.0 | 37.4 | 7.1 | 68.3 | 3345 | 152.2 | 280.6 | 411 |
| **F2** | Average | 5.2 | 19.5 | 5.5 | 36.0 | 2924 | 122.4 | 273.9 | 411 |
| | SD | 3.4 | 7.1 | 1.2 | 12.2 | 619 | 15.3 | 105.0 | 102 |
| | Minimum | < 0.1 | 11.7 | 4.3 | 17.2 | 1931 | 88.7 | 156.6 | 293 |
| | Maximum | 9.0 | 31.7 | 7.8 | 50.9 | 3874 | 135.9 | 432.5 | 579 |
| **ES** | Average | 20.7 | 55.2 | 18.7 | 126.3 | 4309 | 427.8 | 48.6 | 502 |
| | SD | 11.5 | 13.0 | 12.1 | 39.5 | 704 | 197.1 | 50.0 | 211 |
| | Minimum | 9.0 | 37.4 | 6.5 | 92.0 | 3405 | 188.0 | <6.0 | 224 |
| | Maximum | 34.5 | 68.2 | 34.4 | 180.2 | 4963 | 653.0 | 118.7 | 735 |

In Home 3, concentrations of $\Sigma_7$tri-hepta-BDEs, BEH-TEBP and $\Sigma_5$NBFRs ranged between 3.0- 167, 309- 8,051 and 412- 8,309 ng/g respectively, with the highest concentrations found in elevated surface dust sampled in the adult bedroom (H3R2). Concentrations of BDE-209 ranged from 2,023 to 19,802 ng/g, with the highest concentration found in living room floor dust (H3R1). Levels of EH-TBB ranged between 5.3- 63 ng/g, with the highest concentration found in elevated surface dust from the child's bedroom (H3R3), while those of DBDPE varied between < dl and 574 ng/g with the highest concentration found in floor dust from the same room. Tables 3.8, 3.9 and 3.10 summarise concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, EH-TBB, BEH-TEBP and $\Sigma_5$NBFRs in dust samples from two floor areas (F1and F2) and elevated surface dust (ES) from the living room and two bedrooms of Home 3.

**Table 3.8: Concentrations (ng/g) of $\Sigma_7$tri-hepta-BDEs, BDE-209, EH-TBB, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in indoor dust from two floor areas (F1 and F2) and elevated surface (ES) dust samples in the living room of Home 3 (H3R1)**

| Sampling area | Parameter | $\Sigma_7$tri-hepta-BDEs | BDE-209 | EH-TBB | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|---|---|
| F1 | Average | 32.7 | 5639 | 11.4 | 1371 | 162.6 | 1553 |
| | SD | 12.3 | 5323 | 10.7 | 547 | 169.4 | 537 |
| | Minimum | 9.8 | 3152 | < 0.5 | 510 | < 6.0 | 694 |
| | Maximum | 50.5 | 19802 | 28.8 | 2463 | 428.1 | 2492 |
| F2 | Average | 30.2 | 4403 | 9.5 | 926 | 36.7 | 976 |
| | SD | 18.3 | 1732 | 6.9 | 458 | 29.4 | 448 |
| | Minimum | 4.6 | 3243 | < 0.5 | 309 | < 6.0 | 412 |
| | Maximum | 57.6 | 8901 | 20.0 | 1576 | 100.6 | 1621 |
| ES | Average | 64.2 | 3568 | 16.4 | 4187 | 11.0 | 4274 |
| | SD | 35.6 | 378 | 4.5 | 2004 | 10.0 | 2004 |
| | Minimum | 27.1 | 3023 | 12.3 | 2626 | 6.0 | 2681 |
| | Maximum | 109.9 | 3865 | 22.4 | 7129 | 26 | 7207 |

**Table 3.9: Concentrations (ng/g) of $\Sigma_7$tri-hepta-BDEs, BDE-209, EH-TBB, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in indoor dust from two floor areas (F1 and F2) and elevated surface (ES) dust samples in the adult bedroom of Home 3 (H3R2)**

| Sampling area | Parameter | $\Sigma_7$tri-hepta-BDEs | BDE-209 | EH-TBB | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|---|---|
| **F1** | Average | 17.5 | 4252 | 15.3 | 2486 | 95.2 | 2622 |
| | SD | 12.5 | 249 | 7.7 | 880 | 131.5 | 841 |
| | Minimum | 3.0 | 3778 | 5.3 | 1570 | < 6.0 | 1770 |
| | Maximum | 36.3 | 4539 | 29.5 | 4366 | 365.5 | 4476 |
| **F2** | Average | 35.7 | 4129 | 10.4 | 2362 | 68.8 | 2462 |
| | SD | 19.1 | 389 | 6.5 | 1179 | 53.5 | 1162 |
| | Minimum | 6.7 | 3186 | < 0.5 | 765 | 11.4 | 796 |
| | Maximum | 62.8 | 4459 | 21.6 | 4833 | 152.2 | 4898 |
| **ES** | Average | 83.2 | 8451 | 38.3 | 5397 | 45.3 | 5635 |
| | SD | 72.1 | 2124 | 13.9 | 1821 | 18.0 | 1829 |
| | Minimum | 13.7 | 6353 | 22.9 | 4066 | 21.7 | 4300 |
| | Maximum | 167.0 | 10396 | 55.1 | 8051 | 64.9 | 8310 |

**Table 3.10: Concentrations (ng/g) of $\Sigma_7$tri-hepta-BDEs, BDE-209, EH-TBB, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in indoor dust from two floor areas (F1 and F2) and elevated surface (ES) dust samples in the child's bedroom of Home 3 (H3R3)**

| Sampling area | Parameter | $\Sigma_7$tri-hepta-BDEs | BDE-209 | EH-TBB | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|---|---|
| F1 | Average | 37.0 | 4498 | 14.1 | 3046 | 109.4 | 3199 |
| | SD | 15.8 | 190 | 7.9 | 1005 | 122.5 | 944 |
| | Minimum | 19.4 | 4272 | 6.6 | 1882 | 9.0 | 2129 |
| | Maximum | 67.6 | 4773 | 30.7 | 4705 | 387.7 | 4769 |
| F2 | Average | 24.5 | 4401 | 17.5 | 3044 | 116.4 | 3201 |
| | SD | 8.7 | 222 | 7.6 | 982 | 184.5 | 901 |
| | Minimum | 9.8 | 4163 | 6.3 | 1761 | 13.6 | 2014 |
| | Maximum | 39.9 | 4750 | 29.2 | 4696 | 573.8 | 4798 |
| ES | Average | 57.1 | 7138 | 54.4 | 7049 | 48.3 | 7559 |
| | SD | 13.4 | 2135 | 11.9 | 609 | 29.7 | 405 |
| | Minimum | 38.2 | 5619 | 37.6 | 6444 | <6 | 7107 |
| | Maximum | 69.1 | 10302 | 63.4 | 7823 | 61.9 | 8076 |

### 3.3.3 Within-room spatial variation in concentrations of PBDEs and NBFRs

A small number of studies have investigated the implications for estimates of human exposure of within-room spatial variability of concentrations of BFRs in indoor dust (Harrad et al. 2008a; 2009; 2010b; Muenhor and Harrad 2012). In order to obtain a representative sample for human exposure assessment, it has been suggested that the entire floor surface of a room must be sampled (Harrad et al., 2008a). In addition, sampling the most-frequented area of the room is likely to provide the most "biologically relevant" sample (Harrad, 2010b). In the present study, within-room spatial variation in concentrations of PBDEs and NBFRs was investigated in floor dust from two different areas in nine separate rooms over nine months. However, accurate exposure assessments of contaminants via dust ingestion require knowledge about locations where people spend most of their time. Previous studies that base estimates of exposure via dust ingestion on floor dust only, may underestimate exposure. We believe such underestimation is more likely for adults who are in contact with elevated

surfaces such as tables, desk and shelves more than the floor. To the best of the author's knowledge, the data reported in this study are the first to investigate within room spatial variation of PBDEs and NBFRs in dust from floors and elevated surfaces.

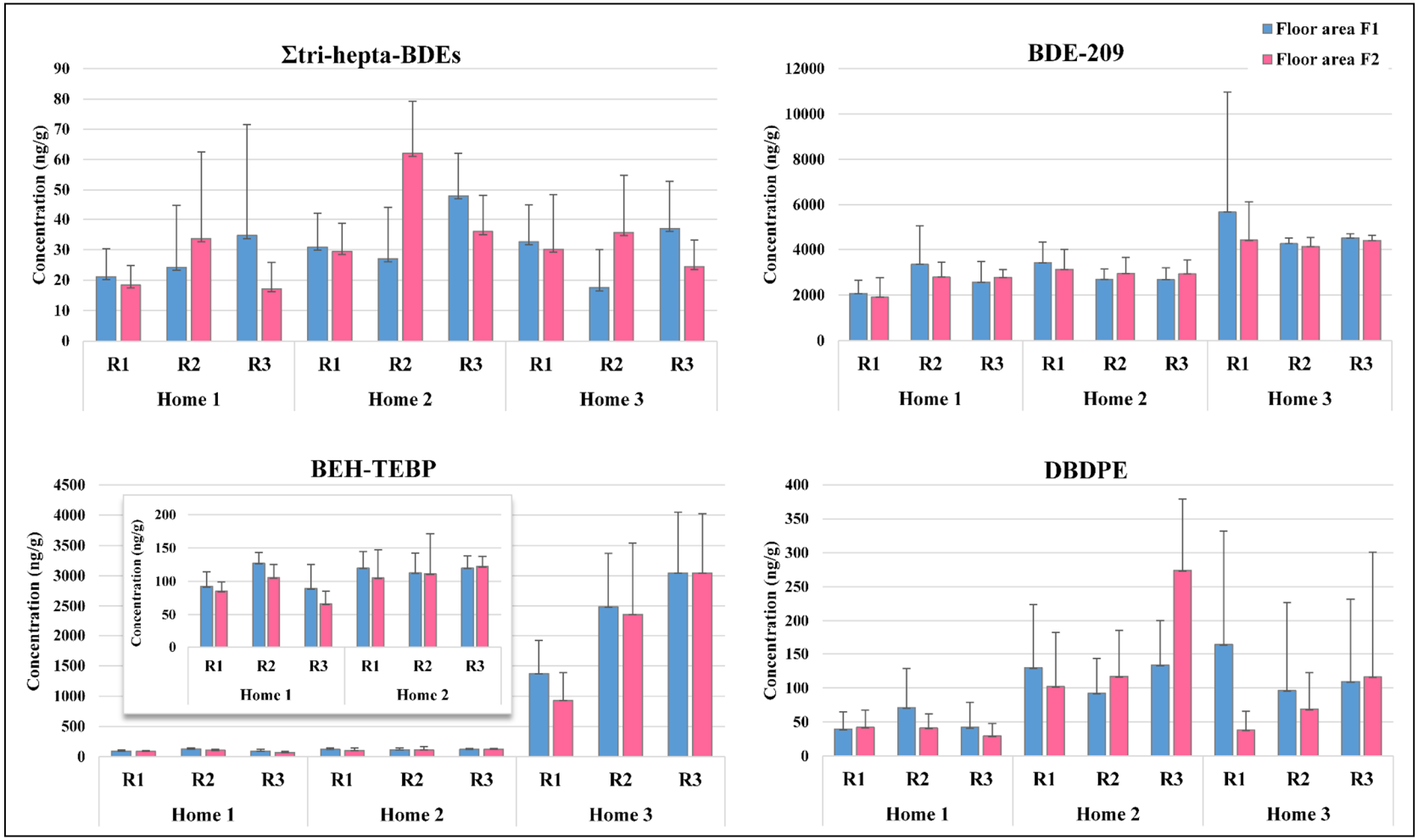
Statistical significance was examined after applying the Shapiro–Wilk test for normality, which revealed that the data are normally distributed. In the nine investigated rooms, t-tests were applied to evaluate within-room spatial variation in concentrations of $\Sigma_7$tri-hepta-BDEs, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in: a) floor dust from two different areas, and b) floor dust and elevated surface dust. In view of the smaller number of elevated surface dust samples (resulting from 2-3 months' worth of samples being combined for analysis due to the low dust loadings of elevated surface dust) compared to floor dust samples; comparison of elevated surface samples with floor dust samples was performed using the average of the concentrations detected in floor dust samples from the matching number of months.

#### 3.3.3.1 Within-room spatial variation of PBDEs and NBFRs in floor dust from two different areas.

Within the same room, paired t-tests were used to examine any significant differences in BFR concentrations in dust samples from different floor areas (F1 and F2 in Figures 3.1, 3.2 and 3.3). This statistical analysis revealed no significant within-room variation in floor dust concentrations of BDE-209 in any of the nine rooms sampled, with $p$ values ranging from 0.109 to 0.576. However, in a few rooms, significant differences were observed in concentrations of $\Sigma_7$tri-hepta-BDEs, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs. In the bedroom of Home 1, concentrations of BEH-TEBP, DBDPE and consequently $\Sigma_5$NBFRs in samples from F1 exceeded significantly those from F2, with $p$ values of 0.012, 0.053 and 0.006 respectively. As shown in Figure 3.1 (H1R2), F1 is the rug area closest to the iron, foam chair, and the curtain, while F2 is the bare floor area located closest to the door and further away (≈ 3 m) from these potential emission sources. In the bedroom of Home 2 (Figure 3.2, H2R2), $\Sigma_7$tri-hepta-BDEs from the floor area F2 closer to the curtain and mattress exceeded significantly ($p < 0.001$) those from floor area F1 closest to the door and located 2.5 m from the potential emission sources. In the same home (H2), concentrations of $\Sigma_7$tri-hepta-BDEs in dust from floor area F1 in the study (Figure 3.2, H2R3) closer to the laptop, printer and foam chair, exceeded significantly ($p = 0.006$) those in floor area F2 which was about 2.7 m from the mentioned potential sources and close to the kitchen door. On the other hand, in the

same room (H2R3), concentrations of DBDPE in the floor area F2 exceeded significantly ($p$ = 0.001) those in floor area F1, which implies that the mentioned products (laptop and the printer) are not the direct emission source of DBDPE due to the low vapour pressure, with the vacuum cleaner and kitchen possible alternative sources (Figure 3.2, H2R3). In the living room of Home 3 (Figure 3.3, H3R1), moderate statistical differences were found between BFR concentrations in the two floor areas. DBDPE and $\Sigma_5$NBFR levels in dust samples from floor area F1 exceeded significantly those from floor area F2, with $p$ values of 0.055 and 0.024 respectively. As shown in Figure 3.3, area F1 contains a rug and is located between the sofas and the TV, while area F2 is bare floor. However, this moderate difference is likely due to placing a new carpet in F2 after the 4$^{th}$ month of sampling, which coincided with an elevation in NBFR concentrations in this area. In addition, in Home 3, concentrations of $\Sigma_7$tri-hepta-BDEs in dust samples from floor area F1 in the adult bedroom (Figure 3.3, H3R2), exceeded significantly ($p$ = 0.052) those from floor area F2 in the same room. As shown in Figure 3.3, F1 was adjacent to the laptop, curtain and foam chair, while F2 is closest to the door further away from the potential emission sources. Figure 3.6 illustrates average concentrations of the most frequently detected compounds ($\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and DBDPE) in floor areas F1 and F2 in the three rooms (R1, R2 and R3) of Home 1, Home 2 and Home 3, along with standard deviation (y error bar). Appendix 2 shows $p$ values obtained from t-test comparison of concentrations of our target compounds in floor dust samples within the same room.

**Figure 3.6: Average concentrations (ng/g) of Σ$_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and DBDPE in dust from different floor (F1 and F2) areas from different rooms (R1 = Living room, R2= Bedroom, and R3 = Study, except in Home 3= Bedroom) in Homes 1, 2, and 3. y-error bars denote 1 standard deviation**



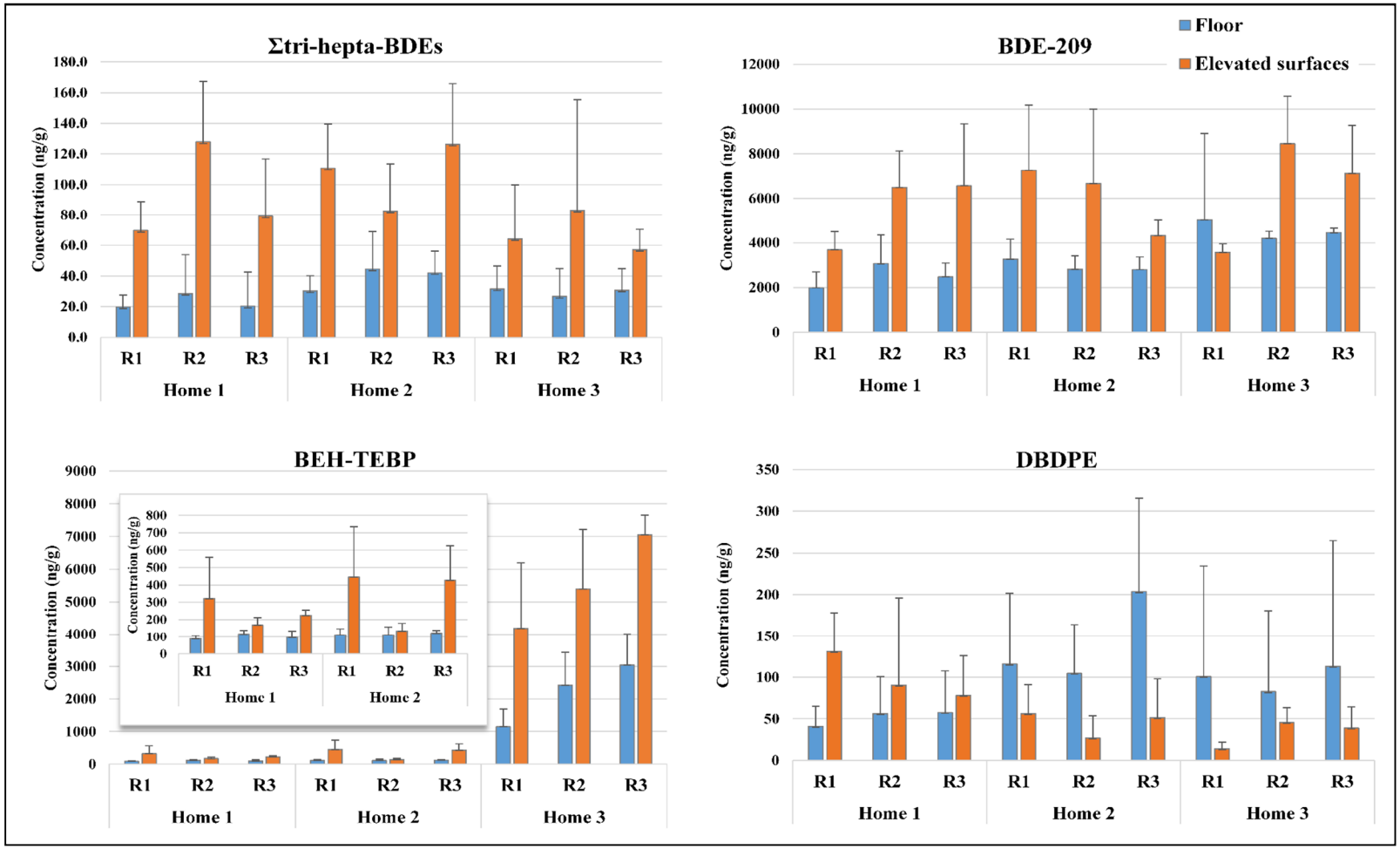
These findings indicate that appreciable variation in BFR contamination can be found depending on where in a given room floor dust samples are taken. The main factors influencing the concentration of our target contaminants in different floor areas are likely to be distance from potential emission sources, whether the area is carpeted or not and the room dimensions. In two rooms, concentrations of $\Sigma_7$tri-hepta-BDEs were significantly higher in dust samples collected from areas closest to foam furniture and electrical equipment (H2R3 Figure 3.2 and H3R2 Figure 3.3). Moreover, concentrations of DBDPE were higher in dust samples from carpeted areas (H1R2 Figure 3.1 and H3R1 Figure 3.3). In addition, room dimensions and consequently the distance between the two floor dust samples may also lead to significant within-room variation. This is illustrated by the absence of significant within-room variation in BFR concentrations in three of the smallest rooms; specifically two living rooms (H1R1 and H2R1) and one study (H1R3). This suggests that the floor area sampled should increase with increasing room area.

Our findings are consistent with previous studies. Within- room spatial variability in contamination of dust with BFRs was first studied by Harrad et al. (2008a). The study showed, in three homes and two offices, that spatial variability in concentrations of tri-hexa-BDEs in dust within the same room, exceeded substantially that attributable to analytical variability. Subsequently, within-room spatial variability in the concentrations of HBCDs in dust was studied in three homes and three offices Harrad et al., (2009). Substantial variability was detected in some rooms, while in others it was minimal. The same authors reported that ΣHBCD concentrations declined sharply with increasing distance from a TV, identified as a likely HBCD source (Harrad et al., 2009). A later study by Muenhor and Harrad (2012), investigated the spatial variability of $\Sigma_{10}$tri-hexa-BDEs in 14 floor areas from six separate rooms in two UK homes. The study reported that “in one room, concentrations of PBDEs in an area located close to putative PBDE sources (TV, laptop, chair and sofa) exceeded substantially those in an area 2 m away, with marked differences also observed between two areas in another room” (Muenhor and Harrad 2012). The consensus of these studies is that room contents, floor covering type and sample location relative to putative influence the concentration of BFRs in indoor floor dust.

### 3.3.3.2 Within-room spatial variation of PBDEs and NBFRs in floor and elevated surface dust

Within-room spatial variation in concentrations of PBDEs and NBFRs was investigated in floor dust and elevated surface dust in three rooms in each of Home 1, Home 2 and Home 3. Taking all 9 investigated rooms together, concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and $\Sigma_5$NBFRs in elevated surface dust exceeded significantly ($p$ = < 0.001) those in floor dust. The one exception to this is that concentrations of DBDPE in floor dust exceeded significantly ($p$ = 0.015) those in elevated surfaces. On an individual room basis, concentrations of $\Sigma_7$tri-hepta-BDEs in elevated surface dust exceeded significantly those in floor dust with $p$ values of 0.022, 0.030, 0.046, 0.007, 0.056, 0.041 and 0.042 in H1R1, H1R2, H1R3, H2R1, H2R2, H2R3 and H3R3 respectively (Figures 3.1, 3.2 and 3.3). Concentrations of BDE-209 in elevated surface dust exceeded significantly those in floor dust with $p$ values of 0.049, 0.042, 0.013 and 0.030 in H1R1, H1R2, H2R3 and H3R2 respectively. In addition, in H1R3, concentrations of BDE-209 concentrations in elevated surfaces dust exceeded (moderate) significantly those in floor dust with a $p$ value of 0.058. Concentrations of BEH-TEBP in elevated surface dust exceeded significantly those in floor dust with $p$ values of 0.025, 0.048, 0.047, 0.040 and 0.008 in H1R3, H2R3, H3R1, H3R2 and H3R3 respectively. Meanwhile, concentrations of DBDPE in floor dust exceeded significantly those in elevated surface dust with $p$ values of 0.026, 0.012, 0.001 and 0.016 in H1R1, H2R2, H2R3 and H3R1 respectively. Finally, $\Sigma_5$NBFR concentrations in elevated surface dust were significantly greater than those in floor dust in H1R3, H3R2 and H3R3 with $p$ values of 0.003, 0.037 and 0.003 respectively, and moderately significant ($p$ = 0.056) in H3R1. Overall, with the exception of DBDPE, average concentrations of BFRs in elevated surface dust were higher than those in corresponding floor dust samples. Figure 3.7 illustrates average concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and DBDPE in floor dust and elevated surface dust in the three different rooms (R1, R2 and R3) of Home 1, Home 2 and Home 3, along with standard deviation (y error bar). Appendix 3 shows the $p$ values obtained for our t-test comparison of concentrations of our target compounds between elevated surface dust and floor dust samples.

**Figure 3.7: Average concentrations (ng/g) of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and DBDPE in floor dust and elevated surface dust from different rooms (R1 = Living room, R2= Bedroom, and R3 = Study, except in Home 3= Bedroom) in Home 1, Home 2 and Home 3. y-error bars denote 1 standard deviation**



Significant positive linear correlations were found between concentrations of BEH-TEBP ($R$ = 0.936; $p$ = < 0.001) and $\Sigma_5$NBFRs ($R$ = 0.914; $p$ = < 0.001) concentrations in paired samples of floor dust and elevated surface dust, while the other contaminants were not significantly correlated. This indicates that while the same emission source(s) appear to influence concentrations of NBFRs levels in both elevated surface dust and floor dust; this is not the case for PBDEs and DBDPE.

The release of SVOCs (including flame retardants) in treated products into indoor dust can occur via one or more of three principal processes. For less brominated contaminants such as $\Sigma_7$tri-hepta-BDEs possessing comparatively higher vapour pressures, the predominant process is likely evaporation from treated articles followed by subsequent atmospheric deposition to settled dust particles (Harrad and Hunter 2006; Cequier et al., 2014; Weschler, and Nazaroff, 2010). This process is less likely to affect transfer of less volatile higher brominated flame retardants such as BDE-209 and DBDPE. For these and other compounds possessing very low vapour pressures, other transfer processes such as abrasion of particles/fibres of source items, along with transfer via direct contact between dust and treated products, are more likely mechanisms effecting transfer to dust (Suzuki et al., 2009; Webster et al., 2009; Harrad et al., 2010b; Rauert et al., 2014a). This may explain why concentrations of $\Sigma_7$tri-hepta-BDEs were higher in elevated surface as opposed to floor dust, while those of DBDPE were greater in floor dust than elevated surface dust. A detailed discussion of this may be found in (discussion in Chapter 5, section 5.3.3 and Chapter 7, section 7.5.4).

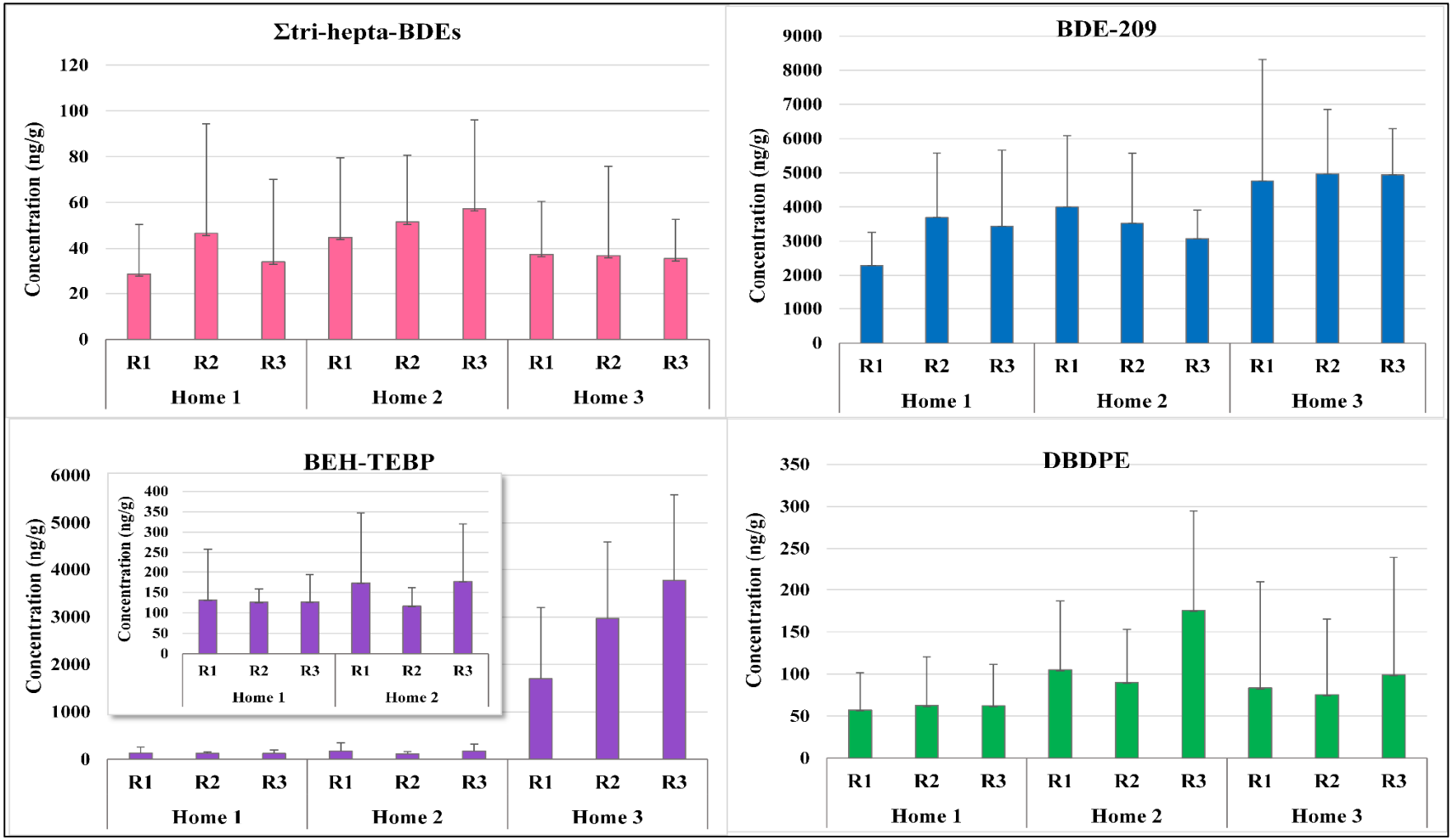
### 3.3.4 Within-home spatial variation in concentrations of PBDEs and NBFRs

Within- home spatial variation in concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs were investigated in three rooms in each of three homes. To facilitate this comparison, we used the average concentrations of BFRs in the two floor areas (F1 and F2) studied in each room. These concentrations were analysed together with elevated surface dust concentrations. After testing our data for normality of distribution (data were found to be log-normally distributed, the skewed distribution data were log-transformed and analysed using repeated measures analysis of variance (ANOVA).

The results of this statistical analysis revealed that in some cases, concentrations of some contaminants differ significantly between rooms in the same home. In Home 1,

concentrations of BDE-209 in the bedroom (H1R2) exceeded significantly those in the living room (H1R1) with a *p* value of 0.010, while for other BFRs, no significant differences were found between different rooms. In Home 2, concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, and DBDPE displayed significant differences between different rooms of the same house. Concentrations of $\Sigma_7$tri-hepta-BDEs in the study (H2R3) exceeded significantly ($p = 0.050$) those in the living room (H2R1). In reverse, BDE-209 concentrations in the living room exceeded significantly ($p = 0.033$) those in the study, while BEH-TEBP and DBDPE concentrations in the study exceeded significantly those in the bedroom with *p* values of 0.041, 0.001 respectively. Meanwhile, in Home 3, significant differences were found between concentrations of BEH-TEBP in the two bedrooms and living room. This home displayed the highest BEH-TEBP concentrations of the three investigated homes. Concentrations of BEH-TEBP in the child's bedroom (H3R3) exceeded significantly those in both the adult bedroom (H3R2) and the living room (H3R1), with *p* values of 0.007 and < 0.001 respectively. At the same time, concentrations of BEH-TEBP in the adult bedroom exceeded significantly those in the living room with a *p* value of < 0.001. Figure 3.8 illustrates within-home spatial variability in concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209 and BEH-TEBP and DBDPE in the three investigated homes.

**Figure 3.8: Average concentrations (ng/g) of Σ$_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and DBDPE in dust from different rooms (R1 = Living room, R2= Bedroom, and R3 = Study, Home 3 = Bedroom) within the same home in Home 1, Home 2 and Home 3. y-error bars denote 1 standard deviation**



Only a few other studies have investigated within home spatial variability. Allen et al., (2008) reported within-home spatial variability in PBDE concentrations in 20 US homes. The study found that PBDE concentrations in the main living area were significantly higher than those in the bedroom with *p* values of 0.05 and 0.02 for Penta-BDE and Deca-BDE respectively, while no significant differences were apparent for Octa-BDE ($p = 0.13$). The same study mentioned that this spatial variability in concentrations of Penta- and Deca-BDE were likely attributable to variation in room-specific sources such as TVs and sofas (Allen et al., 2008). Our findings are consistent with this; for example, concentrations of BDE-209 in the bedroom of H1 exceeded significantly those in the living room, while in H2, concentrations in the study were significantly higher than the living room. At the same time, no significant differences were observed between concentrations of BDE-209 levels in the bedroom and the living room of H3. In another study, Muenhor and Harrad, (2012) concluded that concentrations of PBDEs in separate rooms within the same home can vary quite markedly. Within two UK homes, substantial within-home differences were found. In one home, $\Sigma_{10}$tri-hexa-BDE concentrations in one bedroom (average =340 ng/g) exceeded substantially those in the other bedroom (average = 170 ng/g).

In H2, concentrations of $\Sigma_7$tri-hepta-BDEs in the study were significantly higher than those in the living room. These findings are consistent with other studies reporting higher concentrations of Penta-BDEs in offices than in homes (Harrad et al., 2008a; 2006), as the specific sources in the study of H2 (laptop and printer, Figure 3.2) are similar to those likely to be more prevalent in offices than living rooms of homes. Meanwhile, concentrations of $\Sigma_7$tri-hepta-BDEs, BEH-TEBP and DBDPE in the study exceeded those in the bedroom. Concentrations of BEH-TEBP were highest in H3, which we hypothesise may be due to the new furnishing of this home, particularly in the bedrooms. BEH-TEBP concentrations in H3 fall in the order of: child's bedroom > adult's bedroom > living room. The high levels in the bedrooms might be due to the new mattresses that may have been treated with BEH-TEBP. However, there is no obvious reason for the high concentrations of BEH-TEBP in the child's bedroom compared with adult's bedroom.

## 3.4 The impact of spatial variability on human exposure assessments

To evaluate to what extend that human exposure to our target contaminants via dust ingestion are affected by spatial variability, we compared the mean ± SD concentration in dust samples that collected from: 1) different floor areas in the same room, 2) elevated surfaces and floor in the same room and 3) different rooms in the same home.

As observed in Figure 3.6, substantial differences were appeared in concentrations of BFRs between the two floor areas (F1 and F2), particularly for $\Sigma_7$tri-hepta-BDEs and DBDPE. For examples, in H2R2, concentrations of $\Sigma_7$tri-hepta-BDEs in floor area F2 (average ± SD = 62 ± 17 ng/g) exceeded substantially those in floor area F1 (average ± SD = 27 ± 17 ng/g). In this room, a worst-case was appeared when F1:F2 = 61:4, implying that exposure assessment in that room would vary by a factor of 15 depending on the sampling area. In H3R1, concentrations of DBDPE in floor area F1 (average ± SD = 163 ± 169 ng/g) exceeded substantially those in floor area F2 (average ± SD = 37 ± 29 ng/g). A worst-case was found when F1:F2 = 428:33, implying that exposure assessment in that room would vary by a factor of 13 depending on the sampling area.

Substantial within-room spatial variability was appeared in BFR concentrations between elevated surface dust and floor dust in the nine rooms studied (Figure 3.7). For instant, in H1R2 concentrations of $\Sigma_7$tri-hepta-BDEs in elevated surface dust (average ± SD = 128 ± 39 ng/g) exceeded substantially those in floor dust (average ± SD = 28 ± 15 ng/g). A worst-case was found when ES: F = 15, implying that exposure assessment in that room would vary by a factor of 15 depending on the sampling surface. In H2R1, concentrations of BDE-209 in elevated surface dust (average ± SD = 7269 ± 2908 ng/g) exceeded substantially those in floor dust (average ± SD = 3269 ± 887 ng/g), and the exposure assessments would be vary by a factor of 4.1 depending on the sampling surface. The same relationship was found for BEH-TEBP in H3R1. BEH-TEBP concentrations in elevated surface dust (average ± SD = 4187 ± 2004 ng/g) exceeded substantially those in floor dust (average ± SD = 1196 ± 301 ng/g), a worst-case was found that exposure assessment would be vary by a factor of 5.

BFR concentrations in separate rooms in the same house can differ quite markedly (Figure 3.8). Concentrations of BEH-TEBP in H3R3 (average ± SD = 3992 ± 1906 ng/g) exceeded those in H3R1 (average ± SD = 1811 ± 1498 ng/g). Meanwhile, concentrations of DBDPE

in H3R2 (average ± SD = 176 ± 119 ng/g) exceeded those in H3R1 (average ± SD = 83 ± 63 ng/g). As mentioned in section 3.3.4 that higher concentrations of BEH-TEBP in H3R3 may be related to the new furnishing of the bedrooms, while the reason for the higher concentrations of DBDPE in H3R2 is not clear.

Due to the above substantial within-room and within-home spatial variability, exposure estimates based on one specific floor area, floor surface only or one room may not be entirely representative.

## 3.5 Conclusion and recommendations

This study discussed within-room, and within-home spatial variability in concentrations of PBDEs and NBFRs in dust samples from 3 homes in the UK. Substantial spatial variations in BFR contamination indicate that both floor dust and elevated surface dust should be considered for human exposure assessments, particularly for adults who likely are in contact with elevated surfaces more than the floor. In addition, sampling floor dust from one single area within a room will likely not provide a representative measure of contamination in the room overall, particularly in rooms with large floor areas. To obtain a dust sample from the room representing it as a whole, all elevated surfaces 0.5-1.5 m and more than one floor sample (depending on the room area) should be vacuumed. However, it should be noted that a measurement of BFRs in dust that is representative of a given room is not necessarily the most accurate reflection of human exposure in that room, as sampling all surfaces will include those with which the room occupants have minimal if any contact.

# CHAPTER 4

# WITHIN-ROOM AND WITHIN-HOME TEMPORAL AND SEASONAL VARIABILITY IN CONCENTRATIONS OF PBDEs AND NBFRs IN INDOOR DUST

## 4.1 Summary

To test the hypothesis that temporal variability in PBDEs and NBFRs levels in indoor dust could influence human exposure assessments via dust ingestion, data reported in Chapter 3 were used in this chapter. Within-home and within-room (month-to-month) temporal variability and seasonal (between colder and warmer seasons) variation in concentrations of PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209) and NBFRs (PBEB, EH-TBB, BEH-TEBP, BTBPE and DBDPE) was studied in indoor dust samples from Birmingham, United Kingdom. One elevated surface and two floor dust samples were collected every month from three rooms in each of three homes for nine months. To provide sufficient sample for analysis of elevated surface dust as a consequence of the low dust loadings, 2-3 monthly samples were combined together for elevated surface dust. The BFRs with detection frequencies ≥ 90% and the most common compounds ($\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs) were considered for statistical evaluations.

The relative standard deviations (RSDs) of BFR concentrations in floor dust samples ranged between 12% for BDE-209 to 123% for $\Sigma_7$tri-hepta-BDEs in Home 1, 13% for BEH-TEBP to 88% for BDE-183 in Home 2 and 4% for BDE-209 to 159% for DBDPE in Home 3. RSDs of BFR concentrations in elevated surface dust ranged between 13% for BEH-TEBP to 117% for DBDPE in Home 1, 16% for BDE-209 to 103% for DBDPE in Home 2 and 9% for BEH-TEBP to 91% for DBDPE in Home 3. These RSD values exceeded those obtained from replicate analysis of house dust reference material SRM2585, suggesting that temporal variation exceeds that attributable to analytical variability alone. Likely causes of temporal variability in BFR concentrations include changes in room contents with respect to putative sources of target BFRs. Notwithstanding this, changes in room contents did not appear to explain the gradual decline in concentrations of BEH-TEBP in the bedrooms of Home 3 over the first seven months of sampling.

A t-test was used to assess the seasonal variability in $\Sigma_8$tri-deca-BDEs and $\Sigma_5$NBFRs concentrations in floor dust samples between warmer (spring and summer) and colder (autumn and winter) seasons across all three homes studied. With the exception of two bedrooms (H2R2F1 and H3R3F2 with *p* values of 0.002 and 0.046 respectively), no significant differences in $\Sigma_8$tri-deca-BDEs were found between warmer and colder seasons in floor dust samples. In general, average concentrations of $\Sigma_8$tri-deca-BDEs in 13 out of 17 floor areas were higher in colder seasons than warmer, while in 13 out of 17 areas, average concentrations of $\Sigma_5$NBFRs were higher in warmer seasons than in colder. In four sampling floor areas, $\Sigma_5$NBFR concentrations in warmer seasons exceeded significantly those in colder with *p* values of 0.046, 0.039, 0.051, and 0.023 in H1R1F2, H1R2F1, H3R2F1 and H3R3F1 respectively. It was notable that higher concentrations in colder seasons were only observed for BDE-209 and DBDPE – albeit not in all cases. This may be related to the physicochemical properties (i.e. low volatility) of these BFRs which: (a) favours partitioning to dust from air at lower temperatures and (b) limits emissions from source items via volatilisation.

The aforementioned within-room and within-home temporal and seasonal variability in BFR concentrations, result in variation in exposure assessments depending on when dust sampling is undertaken. The principal influence on temporal and seasonal variability appears to be variations in room contents of putative sources.

## 4.2 Sampling and Sample preparation

From three homes (Home 1, Home 2 and Home 3) in Birmingham, UK, dust samples were collected from three rooms R1 (living room), R2 (bedroom) and R3 (study – child's bedroom in Home 3). From each room, dust samples were collected from two floor areas (F1 and F2) and elevated surfaces (ES) every month for nine months, from May 2013 until March 2014 (with exception of July and August, 2013). Due to the low dust loading on elevated surfaces, 2-3 dust samples were combined together to yield 4 ES dust samples covering 4 durations (D1- D4) over the nine month sampling campaign. Chapter 3, section 3.2 describes our sampling and sample preparation protocols, with Figures 3.1, 3.2 and 3.3 in that chapter showing the contents of each room and the position of each dust sample.

## 4.3 Results and discussion

Limits of detections, relationships between BFRs, and statistical summaries of concentrations, were reported in Chapter 3, sections 3.3.1 and 3.3.2. Only those BFRs with detection frequencies ≥ 90% (for individual homes) and the most common compounds ($\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs) are included in statistical calculations. $\Sigma_7$tri-hepta-BDEs represents the sum of BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, and BDE-183, $\Sigma_8$tri-deca-BDEs represents sum of $\Sigma_7$tri-hepta-BDEs and BDE-209 and $\Sigma_5$NBFRs represents the sum of PBEB, EH-TBB, BTBPE, BEH-TEBP, and DBDPE.

### 4.3.1 Concentrations of PBDEs and NBFRs in indoor dust

Tables 4.1, 4.2, and 4.3 list the concentrations of the most common compounds with detection frequencies ≥ 90% ($\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE, $\Sigma_5$NBFRs, BDE-99 and BTBPE) in each dust sample, together with the corresponding RSD values for the two different floor areas (F1 and F2) sampled in each of the three rooms (R1, R2 and R3) sampled in Home 1. Concentrations of the same BFRs in each combined elevated surface dust sample from each of the three rooms studied in Home 1 are given in Table 4.4. Tables 4.5-4.12 provide the corresponding data for floor and elevated surface dust samples collected from Homes 2 and Home 3.

**Table 4.1: Concentrations (ng/g) of BDE-99, $\Sigma_7$tri-hepta-BDEs, BDE-209, BTBPE, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in dust from two floor areas (F1 and F2) in Home 1, living room (H1R1)**

| Sampling time | BDE-99 | $\Sigma_7$tri-hepta-BDEs | BDE-209 | BTBPE | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|---|---|
| **H1R1F1** | | | | | | | |
| May-13 | 11.8 | 26.2 | 2166 | 15.2 | 96 | 50 | 166 |
| Jun-13 | 9.2 | 17.3 | 2721 | 14.8 | 87 | 24 | 127 |
| Sep-13 | 6.0 | 11.0 | 2135 | 26.7 | 81 | 54 | 187 |
| Oct-13 | 10.1 | 23.5 | 1818 | 8.8 | 90 | 89 | 196 |
| Nov-13 | 14.0 | 29.4 | 3240 | 6.1 | 76 | 14 | 102 |
| Dec-13 | 8.8 | 18.5 | 1645 | 7.1 | 65 | 59 | 133 |
| Jan-14 | 13.6 | 38.6 | 1894 | 17.9 | 138 | 22 | 179 |
| Feb-14 | 7.1 | 16.2 | 1425 | 14.6 | 114 | 30 | 160 |
| Mar-14 | 6.8 | 9.7 | 1505 | 9.8 | 87 | 14 | 112 |
| Average | 9.7 | 21.1 | 2061 | 13.5 | 92 | 40 | 151 |
| SD | 2.9 | 9.2 | 593 | 6.4 | 22 | 25 | 34 |
| % RSD | 30 | 44 | 29 | 48 | 23 | 64 | 22 |
| **H1R1F2** | | | | | | | |
| May-13 | 10.9 | 22.9 | 2871 | 2.4 | 86 | 27 | 119 |
| Jun-13 | 11.8 | 22.0 | 2005 | 23.3 | 87 | 60 | 177 |
| Sep-13 | 7.3 | 12.0 | 1222 | 12.4 | 74 | 73 | 188 |
| Oct-13 | 7.3 | 16.9 | 1638 | 9.2 | 112 | 66 | 189 |
| Nov-13 | 13.7 | 29.9 | 3433 | 6.0 | 82 | 17 | 112 |
| Dec-13 | 6.2 | 11.2 | 970 | 3.4 | 60 | 26 | 91 |
| Jan-14 | 14.2 | 22.6 | 1168 | 4.2 | 86 | 16 | 109 |
| Feb-14 | 3.9 | 11.6 | 2484 | 11.3 | 89 | 21 | 124 |
| Mar-14 | 11.5 | 16.6 | 1321 | 3.0 | 91 | 74 | 171 |
| Average | 9.6 | 18.4 | 1901 | 8.4 | 85 | 42 | 142 |
| SD | 3.6 | 6.4 | 859 | 6.7 | 14 | 25 | 38 |
| % RSD | 37 | 35 | 45 | 80 | 16 | 60 | 27 |

**Table 4.2: Concentrations (ng/g) of BDE-99, $\Sigma_7$tri-hepta-BDEs, BDE-209, BTBPE, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in dust from two floor areas (F1 and F2) in Home 1 bedroom (H1R2)**

| Sampling time | BDE-99 | $\Sigma_7$tri-hepta-BDEs | BDE-209 | BTBPE | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|---|---|
| **H1R2F1** | | | | | | | |
| May-13 | 24.4 | 40.9 | 1824 | 16.0 | 158 | 78 | 252 |
| Jun-13 | < 0.16 | 1.8 | 1008 | 41.2 | 130 | 196 | 367 |
| Sep-13 | 21.8 | 50.9 | 4254 | 14.3 | 126 | 60 | 219 |
| Oct-13 | 27.9 | 53.0 | 3492 | 14.2 | 142 | 131 | 296 |
| Nov-13 | 11.0 | 18.7 | 3277 | 12.0 | 101 | 51 | 179 |
| Dec-13 | 10.1 | 12.5 | 2989 | > 2.8 | 114 | 32 | 146 |
| Jan-14 | < 0.16 | < 0.24 | 3521 | > 2.8 | 123 | 24 | 148 |
| Feb-14 | < 0.16 | < 0.24 | 2653 | > 2.8 | 132 | 35 | 166 |
| Mar-14 | 23.0 | 33.0 | 7064 | 12.9 | 118 | 34 | 168 |
| Average | 13.1 | 23.4 | 3342 | 12.3 | 127 | 71 | 216 |
| SD | 11.4 | 21.6 | 1699 | 12.8 | 16 | 57 | 76 |
| % RSD | 87 | 92 | 51 | 104 | 13 | 80 | 35 |
| **H1R2F2** | | | | | | | |
| May-13 | 7.1 | 7.5 | 2193 | 22.2 | 118 | 45 | 185 |
| Jun-13 | 1.6 | 6.3 | 1628 | 15.2 | 108 | 86 | 210 |
| Sep-13 | 41.6 | 83.7 | 3813 | 6.7 | 101 | 23 | 142 |
| Oct-13 | 35.9 | 69.3 | 3184 | 15.4 | 141 | 54 | 227 |
| Nov-13 | 28.7 | 47.1 | 2883 | 14.2 | 122 | 51 | 187 |
| Dec-13 | 23.4 | 32.5 | 3057 | > 2.8 | 73 | 34 | 109 |
| Jan-14 | 26.2 | 38.4 | 2848 | > 2.8 | 98 | 29 | 126 |
| Feb-14 | 6.9 | 14.3 | 2219 | > 2.8 | 96 | 31 | 127 |
| Mar-14 | < 0.16 | 3.5 | 3255 | 6.4 | 95 | 18 | 120 |
| Average | 19.0 | 33.6 | 2786 | 8.9 | 106 | 41 | 159 |
| SD | 15.5 | 28.9 | 665 | 8.2 | 20 | 21 | 43 |
| % RSD | 81 | 86 | 24 | 92 | 19 | 50 | 27 |

**Table 4.3: Concentrations (ng/g) of BDE-99, $\Sigma_7$tri-hepta-BDEs, BDE-209, BTBPE, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in dust from two floor areas (F1 and F2) in Home 1 study room (H1R3)**

| Sampling time | BDE-99 | $\Sigma_7$tri-hepta-BDEs | BDE-209 | BTBPE | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|---|---|
| **H1R3F1** | | | | | | | |
| May-13 | 3.4 | 5.6 | 2853 | 15.8 | 111 | 39 | 166 |
| Jun-13 | 2.2 | 4.2 | 2208 | 21.4 | 71 | 59 | 152 |
| Sep-13 | 3.3 | 6.1 | 2213 | 57.4 | 149 | 67 | 274 |
| Oct-13 | 11.2 | 28.2 | 1993 | 17.2 | 146 | 104 | 267 |
| Nov-13 | 8.3 | 11.9 | 1476 | 11.7 | 153 | 194 | 358 |
| Dec-13 | 40.0 | 88.2 | 3366 | 72.3 | 61 | 23 | 161 |
| Jan-14 | 15.5 | 30.0 | 3150 | 7.3 | 86 | 20 | 116 |
| Feb-14 | 9.9 | 12.5 | 1376 | 12.8 | 141 | 97 | 252 |
| Mar-14 | 4.3 | 8.3 | 2372 | 21.1 | 69 | 27 | 120 |
| Average | 10.9 | 21.7 | 2334 | 26.3 | 110 | 70 | 207 |
| SD | 11.8 | 26.7 | 689 | 22.6 | 39 | 56 | 83 |
| % RSD | 108 | 123 | 30 | 86 | 35 | 80 | 40 |
| **H1R3F2** | | | | | | | |
| Dec-13 | 11.9 | 22.0 | 2777 | 7.9 | 53 | 57 | 120 |
| Jan-14 | 12.8 | 26.9 | 3077 | 10.2 | 79 | 20 | 113 |
| Feb-14 | 7.5 | 9.3 | 2303 | 20.5 | 47 | 25 | 92 |
| Mar-14 | 6.7 | 10.5 | 2953 | 22.6 | 85 | 16 | 125 |
| Average | 9.7 | 17.2 | 2777 | 15.3 | 66 | 29 | 113 |
| SD | 3.1 | 8.7 | 339 | 7.4 | 19 | 18 | 15 |
| % RSD | 32 | 50 | 12 | 48 | 29 | 62 | 13 |

Note: In H1R3F2 floor area, sampling was conducted for 4 months only.

**Table 4.4: Concentrations (ng/g) of BDE-99, $\Sigma_7$tri-hepta-BDEs, BDE-209, BTBPE, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in dust from elevated surfaces (ES) in Home 1 living room (H1R1), bedroom (H1R2) and study (H1R3)**

| Sampling time | BDE-99 | $\Sigma_7$tri-hepta-BDEs | BDE-209 | BTBPE | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|---|---|
| **H1R1ES** | | | | | | | |
| May+ June+ Sep 13 | 24.4 | 71 | 2475 | 76.3 | 178 | 178 | 446 |
| Oct+ Nov 13 | 34.9 | 74 | 4056 | 45.3 | 183 | 99 | 342 |
| Dec 13 + Jan 14 | 16.3 | 44 | 3850 | 75.8 | 259 | 83 | 435 |
| Feb+ March 14 | 19.5 | 90 | 4334 | 89.1 | 674 | 164 | 936 |
| Average | 23.8 | 70 | 3679 | 71.6 | 323 | 131 | 540 |
| SD | 8.1 | 19 | 827 | 18.6 | 237 | 47 | 268 |
| % RSD | 34 | 28 | 22 | 26 | 73 | 36 | 50 |
| **H1R2ES** | | | | | | | |
| May+ June+ Sep 13 | 61.6 | 103 | 6446 | 11.2 | 223 | 75 | 310 |
| Oct+ Nov 13 | 54.1 | 105 | 7433 | 8.2 | 158 | 35 | 201 |
| Dec 13 + Jan 14 | 66.7 | 117 | 7902 | 6.6 | 115 | 7.7 | 129 |
| Feb+ March 14 | 101 | 186 | 4244 | 5.7 | 177 | 243 | 432 |
| Average | 70.9 | 128 | 6506 | 7.9 | 168 | 90 | 268 |
| SD | 20.9 | 39 | 1626 | 2.4 | 45 | 106 | 132 |
| % RSD | 30 | 31 | 25 | 32 | 27 | 117 | 49 |
| **H1R3ES** | | | | | | | |
| May+ June+ Sep 13 | 17.2 | 29 | 2456 | 40.2 | 241 | 48 | 331 |
| Oct+ Nov 13 | 35.6 | 79 | 8039 | 109 | 188 | 146 | 455 |
| Dec 13 + Jan 14 | 50.3 | 89 | 8319 | 37.3 | 257 | 42 | 345 |
| Feb+ March 14 | 62.4 | 120 | 7476 | 31.9 | 215 | 76 | 329 |
| Average | 41.4 | 79 | 6572 | 54.6 | 225 | 78 | 365 |
| SD | 19.5 | 38 | 2767 | 36 | 30 | 48 | 61 |
| % RSD | 47 | 48 | 42 | 67 | 13 | 61 | 17 |

**Table 4.5: Concentrations (ng/g) of BDE-47, BDE-99, BDE-183, $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in dust from two floor areas (F1 and F2) in Home 1, living room (H2R1)**

| Sampling time | BDE-47 | BDE-99 | BDE-183 | $\Sigma_7$tri-hepta-BDEs | BDE-209 | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|---|---|---|
| **H2R1F1** | | | | | | | | |
| May-13 | 7.8 | 14.7 | 2.7 | 35 | 3218 | 126 | 304 | 442 |
| Jun-13 | 3.8 | 8.1 | 7.4 | 29 | 2526 | 129 | 85 | 220 |
| Sep-13 | < 0.1 | 3.3 | 4.6 | 13 | 5034 | 104 | 64 | 181 |
| Oct-13 | 6.0 | 16.4 | 3.7 | 30 | 2264 | 97 | 232 | 366 |
| Nov-13 | 7.1 | 21.6 | 2.6 | 37 | 2871 | 165 | 207 | 397 |
| Dec-13 | 1.9 | 3.1 | 8.8 | 14 | 2764 | 143 | 110 | 252 |
| Jan-14 | 6.7 | 20.8 | 12.3 | 42 | 3792 | 130 | 38 | 177 |
| Feb-14 | 6.8 | 17.8 | 6.2 | 37 | 3974 | 93 | 67 | 179 |
| Mar-14 | 6.0 | 14.1 | 15.4 | 42 | 4280 | 92 | 61 | 153 |
| Average | 5.1 | 13.3 | 7.1 | 31 | 3414 | 120 | 130 | 263 |
| SD | 2.6 | 7.0 | 4.4 | 11 | 915 | 25 | 94 | 109 |
| % RSD | 52 | 52 | 62 | 36 | 27 | 21 | 72 | 42 |
| **H2R1F2** | | | | | | | | |
| May-13 | 9.4 | 20.7 | 3.0 | 43 | 2578 | 106 | 161 | 276 |
| Jun-13 | 7.0 | 12.3 | 6.7 | 34 | 2302 | 111 | 126 | 249 |
| Sep-13 | < 0.1 | 7.3 | 3.4 | 17 | 3268 | 115 | 89 | 214 |
| Oct-13 | 4.8 | 16.8 | 2.0 | 26 | 1650 | 85 | 51 | 140 |
| Nov-13 | 4.8 | 12.3 | 3.9 | 27 | 3069 | 107 | 135 | 250 |
| Dec-13 | 3.0 | 8.9 | 3.5 | 16 | 2923 | 167 | 262 | 440 |
| Jan-14 | < 0.1 | 4.8 | 21.7 | 28 | 4239 | 151 | 74 | 247 |
| Feb-14 | 6.1 | 14.1 | 12.7 | 39 | 4344 | 18 | 12 | 42 |
| Mar-14 | 3.8 | 16.7 | 8.9 | 36 | 3737 | 86 | 9 | 95 |
| Average | 4.3 | 12.6 | 7.3 | 29 | 3123 | 105 | 102 | 217 |
| SD | 3.1 | 5.1 | 6.4 | 9 | 889 | 42 | 80 | 116 |
| % RSD | 71 | 40 | 88 | 31 | 28 | 40 | 78 | 53 |

**Table 4.6: Concentrations (ng/g) of BDE-47, BDE-99, BDE-183, $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in dust from two floor areas (F1 and F2) in Home 2, bedroom (H2R2)**

| Sampling time | BDE-47 | BDE-99 | BDE-183 | $\Sigma_7$tri-hepta-BDEs | BDE-209 | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|---|---|---|
| **H2R2F1** | | | | | | | | |
| May-13 | 0.5 | 0.4 | < 0.2 | 4 | 2464 | 128 | 43 | 188 |
| Jun-13 | 7.2 | 9.2 | 2.8 | 27 | 1907 | 124 | 194 | 339 |
| Sep-13 | 11.0 | 25.2 | 8.7 | 54 | 2544 | 91 | 31 | 141 |
| Oct-13 | 4.1 | 6.2 | 3.6 | 20 | 2614 | 98 | 91 | 203 |
| Nov-13 | 7.8 | 20.4 | 2.7 | 37 | 2809 | 100 | 91 | 320 |
| Dec-13 | 9.2 | 33.7 | 3.5 | 49 | 2290 | 103 | 139 | 261 |
| Jan-14 | 5.0 | 6.1 | 7.6 | 19 | 3063 | 183 | 94 | 289 |
| Feb-14 | 5.1 | 17.2 | 3.3 | 26 | 3188 | 104 | 101 | 204 |
| Mar-14 | < 0.1 | 1.7 | 2.2 | 8 | 3301 | 84 | 44 | 135 |
| Average | 5.5 | 13.4 | 3.8 | 27 | 2687 | 113 | 92 | 231 |
| SD | 3.7 | 11.4 | 2.7 | 17 | 451 | 30 | 51 | 74 |
| % RSD | 67 | 86 | 70 | 64 | 17 | 27 | 56 | 32 |
| **H2R2F2** | | | | | | | | |
| May-13 | 15.8 | 30.2 | 3.9 | 61 | 2253 | 105 | 106 | 253 |
| Jun-13 | 16.6 | 35.3 | 5.6 | 66 | 3277 | 267 | 174 | 465 |
| Sep-13 | 23.6 | 43.1 | 3.9 | 81 | 2180 | 72 | 57 | 146 |
| Oct-13 | 30.6 | 41.1 | 6.1 | 82 | 1955 | 91 | 156 | 264 |
| Nov-13 | 23.9 | 44.8 | 5.3 | 78 | 3340 | 94 | 226 | 356 |
| Dec-13 | 13.9 | 34.1 | 3.3 | 61 | 2552 | 122 | 171 | 314 |
| Jan-14 | 11.4 | 16.0 | 2.4 | 32 | 3674 | 90 | 58 | 156 |
| Feb-14 | 21.7 | 24.7 | 5.0 | 55 | 3499 | 88 | 73 | 161 |
| Mar-14 | 11.6 | 20.7 | 3.3 | 44 | 3796 | 72 | 31 | 103 |
| Average | 18.8 | 32.2 | 4.3 | 62 | 2947 | 111 | 117 | 247 |
| SD | 6.5 | 10.2 | 1.2 | 17 | 710 | 61 | 67 | 118 |
| % RSD | 35 | 32 | 28 | 28 | 24 | 55 | 57 | 48 |

**Table 4.7: Concentrations (ng/g) of BDE-47, BDE-99, BDE-183, $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in dust from two floor areas (F1 and F2) in Home 2, study room (H2R3)**

| Sampling time | BDE-47 | BDE-99 | BDE-183 | $\Sigma_7$tri-hepta-BDEs | BDE-209 | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|---|---|---|
| **H2R3F1** | | | | | | | | |
| May-13 | 20.0 | 25.5 | 7.1 | 67 | 2584 | 115 | 114 | 232 |
| Jun-13 | 12.0 | 37.4 | 5.9 | 68 | 2320 | 106 | 60 | 197 |
| Sep-13 | 10.6 | 34.1 | 4.6 | 57 | 1789 | 91 | 113 | 218 |
| Oct-13 | 11.3 | 28.2 | 5.6 | 54 | 2626 | 117 | 189 | 316 |
| Nov-13 | 7.5 | 22.9 | 5.5 | 42 | 2932 | 122 | 281 | 411 |
| Dec-13 | 8.3 | 23.1 | 4.6 | 42 | 2165 | 152 | 156 | 317 |
| Jan-14 | 4.6 | 22.1 | 4.4 | 34 | 3276 | 141 | 90 | 240 |
| Feb-14 | 6.0 | 11.9 | 3.2 | 28 | 3009 | 110 | 89 | 199 |
| Mar-14 | 8.8 | 18.5 | 4.3 | 40 | 3345 | 124 | 111 | 255 |
| Average | 9.9 | 24.9 | 5.0 | 48 | 2672 | 120 | 134 | 265 |
| SD | 4.5 | 7.7 | 1.1 | 14 | 521 | 18 | 67 | 70 |
| % RSD | 45 | 31 | 23 | 29 | 19 | 15 | 50 | 27 |
| **H2R3F2** | | | | | | | | |
| May-13 | 7.7 | 23.3 | 7.8 | 51 | 3200 | 117 | 173 | 303 |
| Jun-13 | 6.4 | 21.8 | 6.9 | 42 | 1931 | 109 | 241 | 383 |
| Sep-13 | 9.0 | 31.7 | 5.5 | 48 | 2465 | 89 | 432 | 534 |
| Oct-13 | 8.0 | 27.6 | 5.1 | 47 | 2792 | 127 | 318 | 455 |
| Nov-13 | < 0.1 | 17.5 | 4.3 | 25 | 2693 | 131 | 431 | 579 |
| Dec-13 | < 0.1 | 11.7 | 4.9 | 17 | 2441 | 132 | 292 | 448 |
| Jan-14 | 3.6 | 12.8 | 6.2 | 24 | 3554 | 134 | 172 | 317 |
| Feb-14 | 4.8 | 11.7 | 4.4 | 31 | 3874 | 136 | 157 | 293 |
| Mar-14 | 7.3 | 17.8 | 4.3 | 39 | 3364 | 125 | 249 | 388 |
| Average | 5.2 | 19.5 | 5.5 | 36 | 2924 | 122 | 274 | 411 |
| SD | 3.4 | 7.1 | 1.2 | 12 | 619 | 15 | 105 | 102 |
| % RSD | 65 | 37 | 23 | 34 | 21 | 12 | 38 | 24.7 |

**Table 4.8: Concentrations (ng/g) of BDE-47, BDE-99, BDE-183, $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in dust from elevated surfaces (ES) in Home 2, living room (H2R1), bedroom (H2R1) and study room (H2R3)**

| Sampling time | BDE-47 | BDE-99 | BDE-183 | $\Sigma_7$tri-hepta-BDEs | BDE-209 | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|---|---|---|
| **H2R1ES** | | | | | | | | |
| May+ Jun 13 | 29.6 | 59.6 | 41.7 | 149 | 11105 | 633 | 37 | 695 |
| Sep+ Oct+ Nov 13 | 11.1 | 26.9 | 31.7 | 80 | 5874 | 722 | 98 | 839 |
| Dec 13+ Jan 14 | 16.6 | 38.0 | 40.5 | 101 | 4355 | 338 | 69 | 428 |
| Feb+ March 14 | 22.0 | 49.6 | 26.4 | 114 | 7741 | 87 | 20 | 131 |
| Average | 19.8 | 43.5 | 35.1 | 111 | 7269 | 445 | 56 | 523 |
| SD | 7.9 | 14.2 | 7.3 | 29 | 2908 | 290 | 35 | 312 |
| % RSD | 40 | 33 | 21 | 26 | 40 | 65 | 62 | 60 |
| **H2R2ES** | | | | | | | | |
| May+ Jun 13 | 17.6 | 26.2 | 6.9 | 51 | 8843 | 135 | 10.0 | 145 |
| Sep+ Oct+ Nov 13 | 44.6 | 58.6 | 8.3 | 121 | 10168 | 197 | 66.2 | 279 |
| Dec 13+ Jan 14 | 31.7 | 53.6 | < 0.2 | 93 | 3511 | 114 | 20.8 | 208 |
| Feb+ March 14 | 18.2 | 39.3 | 6.8 | 66 | 4176 | 95 | 9.6 | 115 |
| Average | 28.0 | 44.4 | 5.5 | 83 | 6675 | 135 | 26.7 | 186 |
| SD | 11.4 | 13.3 | 3.6 | 29 | 2722 | 43 | 25.5 | 68 |
| % RSD | 41 | 30 | 66 | 35 | 41 | 32 | 96 | 36 |
| **H2R3ES** | | | | | | | | |
| May+ Jun 13 | 25.7 | 54.8 | 6.5 | 92 | 3405 | 188 | <6.0 | 224 |
| Sep+ Oct+ Nov 13 | 9.0 | 37.4 | 34.4 | 102 | 4756 | 371 | 118.7 | 500 |
| Dec 13+ Jan 14 | 13.7 | 68.2 | 12.7 | 131 | 4111 | 499 | 37.0 | 551 |
| Feb+ March 14 | 34.5 | 60.4 | 21.0 | 180 | 4963 | 653 | 38.8 | 735 |
| Average | 20.7 | 55.2 | 18.7 | 126 | 4309 | 428 | 48.6 | 502 |
| SD | 11.5 | 13.0 | 12.1 | 39 | 705 | 197 | 50.0 | 211 |
| % RSD | 56 | 24 | 65 | 31 | 16 | 46 | 103 | 42 |

**Table 4.9: Concentrations (ng/g) of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in dust from two floor areas (F1 and F2) in Home 3, living room (H3R1)**

| Sampling time | $\Sigma_7$tri-hepta-BDEs | BDE-209 | EH-TBB | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|---|
| **H3R1F1** | | | | | | |
| May-13 | 36.9 | 3931 | 2.5 | 1114 | 428 | 1571 |
| Jun-13 | 44.8 | 3606 | 2.7 | 1556 | 46 | 1609 |
| Sep-13 | 34.0 | 3152 | 6.6 | 1781 | 321 | 2115 |
| Oct-13 | 31.3 | 19802 | 18.3 | 1482 | 76 | 1588 |
| Nov-13 | 50.5 | 3842 | 28.8 | 2463 | < 6.0 | 2492 |
| Dec-13 | 9.8 | 4119 | 3.9 | 1217 | 378 | 1616 |
| Jan-14 | 23.9 | 4429 | 14.3 | 510 | 170 | 694 |
| Feb-14 | 23.4 | 4144 | 25.2 | 1202 | 37 | 1265 |
| Mar-14 | 39.4 | 3728 | < 0.5 | 1011 | 7 | 1024 |
| Average | 32.7 | 5639 | 11.4 | 1371 | 163 | 1553 |
| SD | 12.3 | 5323 | 10.7 | 547 | 169 | 537 |
| % RSD | 38 | 94 | 94 | 40 | 104 | 35 |
| **H3R1F2** | | | | | | |
| May-13 | 49.7 | 3243 | < 0.5 | 1576 | 33 | 1609 |
| Jun-13 | 57.6 | 4452 | 3.4 | 1336 | 24 | 1374 |
| Sep-13 | 24.6 | 3690 | 14.7 | 1567 | 35 | 1621 |
| Oct-13 | 19.9 | 8901 | 9.9 | 820 | < 6.0 | 837 |
| Nov-13 | 4.6 | 3331 | 2.3 | 309 | 101 | 412 |
| Dec-13 | 17.0 | 3850 | 7.3 | 853 | 60 | 920 |
| Jan-14 | 38.1 | 3828 | 10.4 | 583 | 42 | 641 |
| Feb-14 | 14.0 | 4237 | 20.0 | 691 | 22 | 732 |
| Mar-14 | 46.2 | 4096 | 17.3 | 603 | 13 | 633 |
| Average | 30.2 | 4403 | 9.5 | 926 | 37 | 976 |
| SD | 18.3 | 1732 | 6.9 | 458 | 29 | 448 |
| % RSD | 61 | 39 | 73 | 49 | 80 | 46 |

**Table 4.10: Concentrations (ng/g) of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP DBDPE and $\Sigma_5$NBFRs in dust from two floor areas (F1 and F2) in Home 3, bedroom (H3R2)**

| Sampling time | $\Sigma_7$tri-hepta-BDEs | BDE-209 | EH-TBB | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|---|
| **H3R2F1** | | | | | | |
| May-13 | 36.3 | 4055 | 5.3 | 2426 | 56 | 2501 |
| Jun-13 | 35.2 | 4108 | 16.6 | 3132 | 36 | 3202 |
| Sep-13 | 14.1 | 4513 | 23.4 | 4366 | 18 | 4476 |
| Oct-13 | 24.7 | 4350 | 29.5 | 2991 | 17 | 3052 |
| Nov-13 | 4.6 | 4296 | 6.4 | 1570 | 365 | 2014 |
| Dec-13 | 6.0 | 4539 | 10.7 | 1999 | 275 | 2284 |
| Jan-14 | 14.6 | 4462 | 16.9 | 2163 | 75 | 2269 |
| Feb-14 | 3.0 | 4169 | 12.8 | 1993 | < 6.0 | 2027 |
| Mar-14 | 19.3 | 3778 | 15.8 | 1736 | 15 | 1770 |
| Average | 17.5 | 4252 | 15.3 | 2486 | 95 | 2622 |
| SD | 12.5 | 249 | 7.7 | 880 | 131 | 841 |
| % RSD | 71 | 6 | 51 | 35 | 138 | 32 |
| **H3R2F2** | | | | | | |
| May-13 | 39.2 | 3186 | < 0.5 | 2333 | 84 | 2454 |
| Jun-13 | 17.7 | 4459 | 8.1 | 4833 | 11 | 4898 |
| Sep-13 | 20.6 | 4365 | 17.6 | 3251 | 15 | 3293 |
| Oct-13 | 32.7 | 4165 | 14.1 | 2894 | 19 | 2927 |
| Nov-13 | 6.7 | 4035 | 6.0 | 1889 | 152 | 2084 |
| Dec-13 | 31.7 | 4251 | 10.3 | 1858 | 125 | 2003 |
| Jan-14 | 62.8 | 4292 | 21.6 | 1902 | 97 | 2053 |
| Feb-14 | 58.4 | 4423 | 9.0 | 1528 | 95 | 1650 |
| Mar-14 | 51.3 | 3987 | 7.1 | 765 | 20 | 796 |
| Average | 35.7 | 4129 | 10.4 | 2362 | 69 | 2462 |
| SD | 19.1 | 389 | 6.5 | 1179 | 54 | 1162 |
| % RSD | 54 | 9 | 62 | 50 | 78 | 47 |

**Table 4.11: Concentrations (ng/g) of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in dust from two floor areas (F1 and F2) in Home 3, Child's bedroom (H3R3)**

| Sampling time | $\Sigma_7$tri-hepta-BDEs | BDE-209 | EH-TBB | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|---|
| **H3R3F1** | | | | | | |
| May-13 | 67.6 | 4280 | 7.0 | 3982 | 92 | 4215 |
| Jun-13 | 30.1 | 4682 | 30.7 | 4705 | 12 | 4769 |
| Sep-13 | 22.0 | 4335 | 20.3 | 4002 | 9 | 4042 |
| Oct-13 | 35.6 | 4272 | 18.8 | 3349 | 10 | 3400 |
| Nov-13 | 35.8 | 4773 | 6.6 | 1919 | 388 | 2338 |
| Dec-13 | 43.9 | 4466 | 8.8 | 1882 | 211 | 2129 |
| Jan-14 | 53.8 | 4562 | 13.4 | 2596 | 114 | 2748 |
| Feb-14 | 19.4 | 4410 | 10.1 | 2463 | 79 | 2552 |
| Mar-14 | 24.7 | 4700 | 11.1 | 2513 | 70 | 2593 |
| Average | 37.0 | 4498 | 14.1 | 3046 | 109 | 3199 |
| SD | 16 | 190 | 7.9 | 1005 | 123 | 944 |
| % RSD | 43 | 4 | 56 | 33 | 112 | 29 |
| **H3R3F2** | | | | | | |
| May-13 | 25.7 | 4245 | 29.2 | 4696 | 38 | 4798 |
| Jun-13 | 9.8 | 4253 | 23.8 | 4115 | 14 | 4174 |
| Sep-13 | 29.6 | 4163 | 19.5 | 3380 | 26 | 3449 |
| Oct-13 | 26.8 | 4196 | 15.3 | 3106 | 22 | 3157 |
| Nov-13 | 19.3 | 4430 | 6.4 | 2070 | 574 | 2679 |
| Dec-13 | 39.9 | 4750 | 6.3 | 1761 | 236 | 2014 |
| Jan-14 | 18.3 | 4748 | 15.5 | 1993 | 58 | 2083 |
| Feb-14 | 30.7 | 4356 | 22.9 | 3089 | 36 | 3176 |
| Mar-14 | 20.4 | 4469 | 18.4 | 3189 | 45 | 3274 |
| Average | 24.5 | 4401 | 17.5 | 3044 | 116 | 3201 |
| SD | 8.7 | 222 | 7.6 | 982 | 185 | 901 |
| % RSD | 36 | 5 | 44 | 32 | 159 | 28 |

**Table 4.12: Concentrations (ng/g) of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in dust from elevated surface (ES) in Home 3, living room (H3R1), adult bedroom (H3R1) and child's bedroom (H3R3)**

| Sampling time | $\Sigma_7$tri-hepta-BDEs | BDE-209 | EH-TBB | BEH-TEBP | DBDPE | Σ5NBFRs |
|---|---|---|---|---|---|---|
| **H3R1ES** | | | | | | |
| May+ Jun 13 | 72 | 3865 | 12.3 | 7129 | 6.0 | 7207 |
| Sep+ Oct 13 | 110 | 3023 | 17.2 | 3558 | 6.0 | 3672 |
| Nov+ Dec 13 | 27 | 3773 | 22.4 | 3435 | 26.0 | 3537 |
| Jan+ Feb+ March 14 | 48 | 3611 | 13.7 | 2626 | 6.0 | 2681 |
| Average | 64 | 3568 | 16.4 | 4187 | 11.0 | 4274 |
| SD | 36 | 378 | 4.5 | 2004 | 10 | 2004 |
| % RSD | 55 | 11 | 27 | 48 | 91 | 47 |
| **H3R2ES** | | | | | | |
| May+ Jun 13 | 167 | 10396 | 55.1 | 8051 | 50.5 | 8310 |
| Sep+ Oct 13 | 119 | 10162 | 42.9 | 4374 | 21.7 | 4651 |
| Nov+ Dec 13 | 33 | 6353 | 22.9 | 4066 | 64.9 | 4300 |
| Jan+ Feb+ March 14 | 14 | 6895 | 32.4 | 5097 | 44.4 | 5279 |
| Average | 83 | 8451 | 38.3 | 5397 | 45.3 | 5635 |
| SD | 72 | 2124 | 13.9 | 1821 | 18.0 | 1829 |
| % RSD | 87 | 25 | 36 | 34 | 40 | 32 |
| **H3R4ES** | | | | | | |
| May+ Jun 13 | 69 | 10302 | 37.6 | 6707 | <6 | 7625 |
| Sep+ Oct 13 | 63 | 6331 | 63.4 | 7221 | 23.9 | 7430 |
| Nov+ Dec 13 | 38 | 5619 | 62.3 | 6444 | 61.9 | 7107 |
| Jan+ Feb+ March 14 | 58 | 6300 | 54.4 | 7823 | 59.1 | 8076 |
| Average | 57 | 7138 | 54.4 | 7049 | 48.3 | 7559 |
| SD | 13 | 2135 | 11.9 | 609 | 29.7 | 405 |
| % RSD | 23 | 30 | 22 | 9 | 82 | 5 |

### 4.3.2 Within-room and within-home temporal variation in concentrations of BFRs

#### 4.3.2.1 Within-room and within-home temporal variation in concentrations of PBDEs and NBFRs in floor dust.

Within-room and within-home temporal variation of PBDEs and NBFRs was investigated in dust samples from 18 individual floor areas within Home 1, Home 2 and Home 3 every month over nine months from May 2013 until March 2014. In Home 1, as shown in Tables 4.1, 4.2 and 4.3, the RSDs of BFR concentrations in floor dust ranged between 12% of BDE-209 in dust samples collected from area F2 in the study room (H1R3) to 123% of $\Sigma_7$tri-hepta-BDEs in dust samples collected from area F1 in the same room (Figure 3.1, Chapter 3). In Home 2 (Tables 4.5, 4.6 and 4.7), the RSDs ranged between 13% of BEH-TEBP in dust samples from floor area F2 in the study room (H2R3) to 88% of BDE-183 from F2 in the living room (Figure 3.2, Chapter 3). In Home 3 (Tables 4.9, 4.10 and 4.11), RSDs ranged between 4% of BDE-209 area F1 in the child's bedroom (H3R3) to 159% of DBDPE from area F2 in the same room (Figure 3.3, Chapter 3).

In general, these RSD values exceeded those obtained from replicate analysis of house dust reference material SRM2585, which were between 9% - 14% for PBDEs and 14% - 15% in NBFRs (Tables 2.11 and 2.12, Chapter 2). In addition, noticeable variation in maximum: minimum BFR levels were found depending on a given area, particularly for $\Sigma_7$tri-hepta-BDEs and DBDPE. The ratio of maximum: minimum concentrations of $\Sigma_7$tri-hepta-BDEs were 30, 24 and 21, in areas H1R2F1, H1R2F2 and H1R3F1 respectively, and for DBDPE were 28, 71, 61, 43 and 42 in areas H2R1F2, H3R1F1, H3R2F1, H3R3F1, and H3R3F2, respectively. Figures 4.1 and 4.2 and 4.3 illustrate the intra-room temporal variation in concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE, and $\Sigma_5$NBFRs in dust from different floor areas (F1 and F2) from different rooms (R1, R2 and R3) during the nine monitored months in Home 1, Home 2 and Home 3 respectively, along with Table 4.13 lists maximum: minimum concentration ratios of these compounds in floor areas.

**Figure 4.1: Within-room temporal variation in concentrations (ng/g) of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in dust from two floor areas (F1 and F2) in different rooms (R1 = living room, R2 = bedroom and R3 = study) of Home 1**

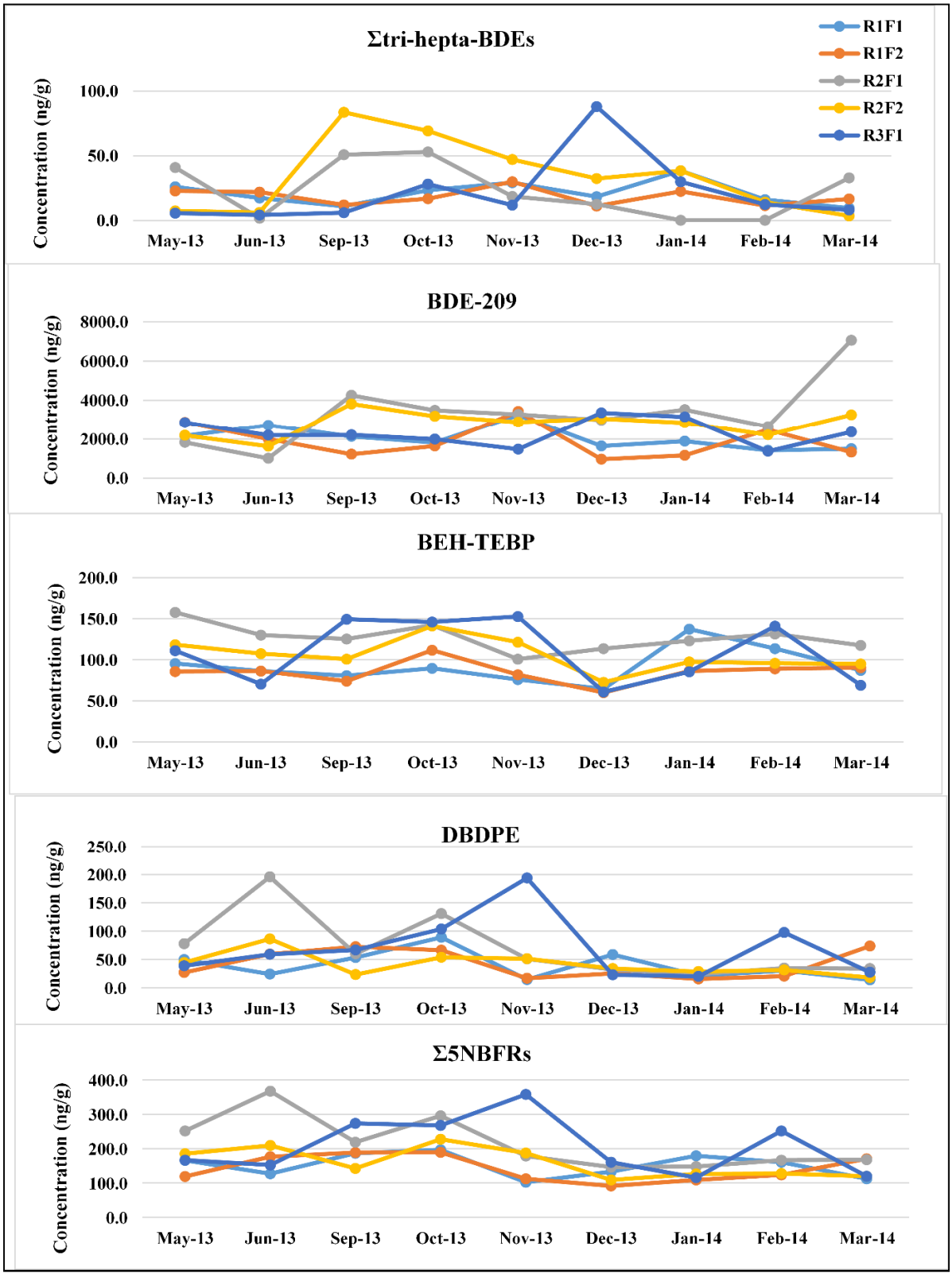


**Figure 4.2: Within-room temporal variation in concentrations (ng/g) of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in dust from two floor areas (F1 and F2) in different rooms (R1 = living room, R2 = bedroom and R3 = study) of Home 2**

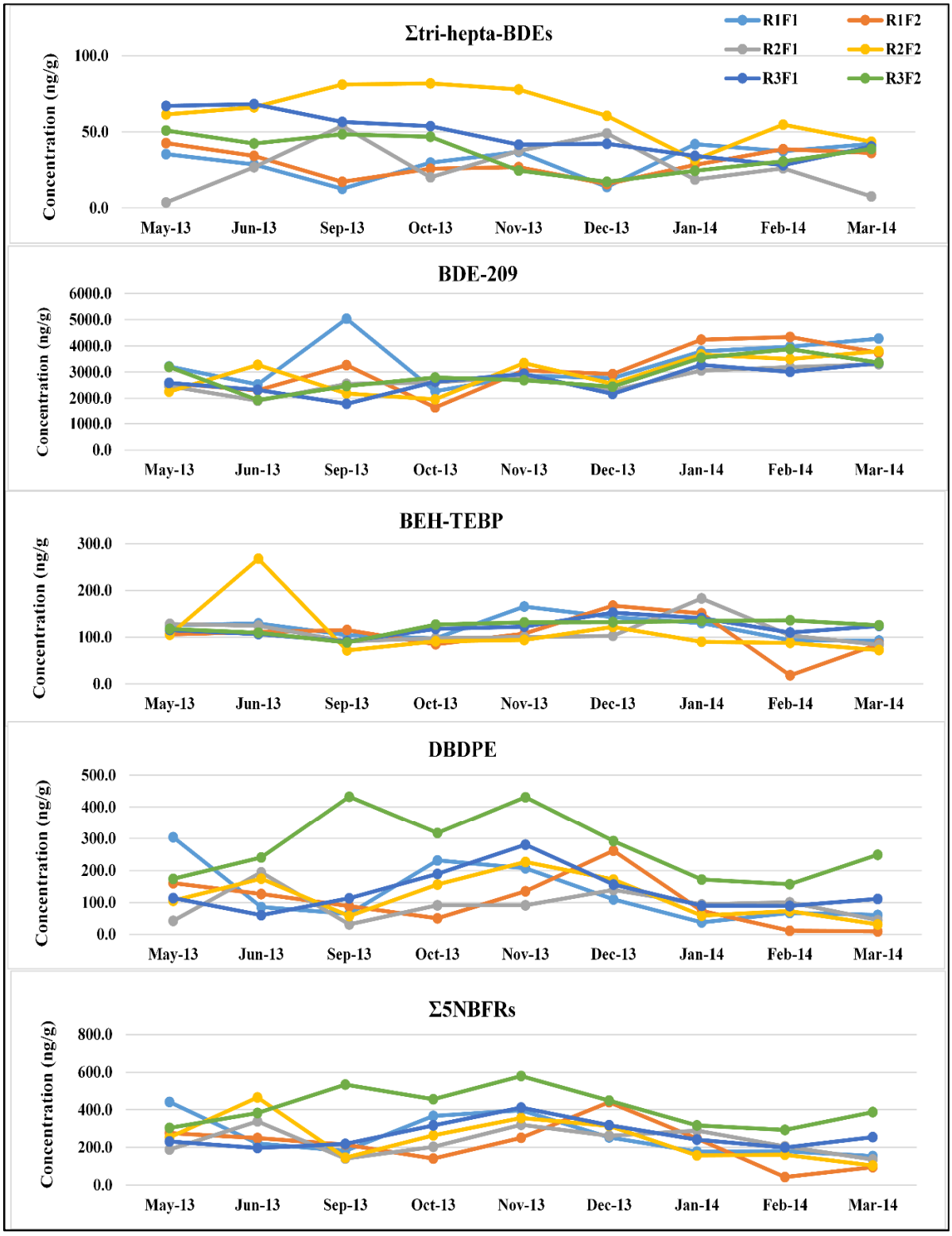


**Figure 4.3: Within-room temporal variation in concentrations (ng/g) of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in dust from two floor areas (F1 and F2) in different rooms (R1 = living room, R2 = adult bedroom and R3 = child's bedroom) of Home 3**

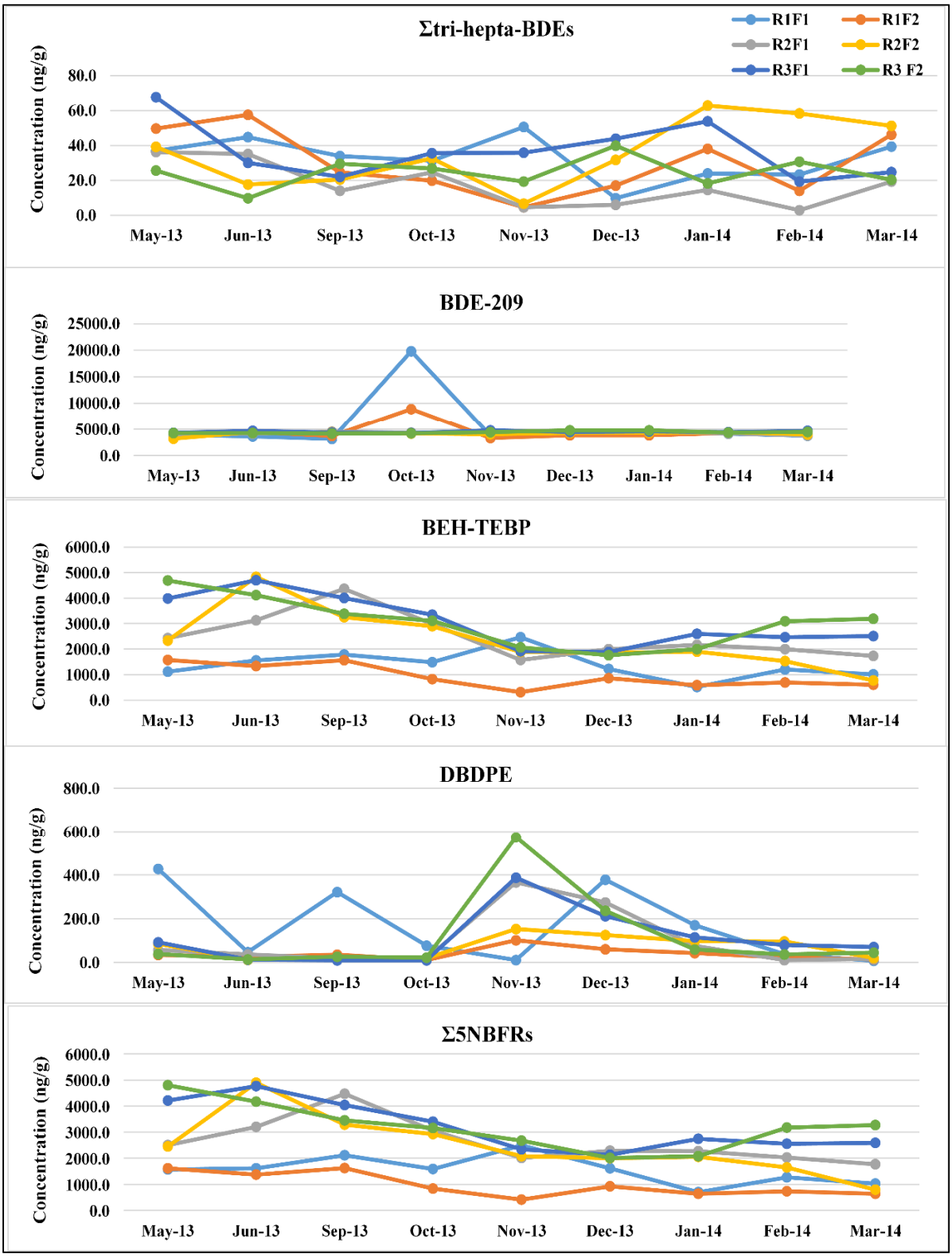


**Table 4.13: Maximum: minimum ratio in concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in floor dust samples (F1 and F2) from three rooms (R1, R2 and R3) in Home1, Home2 and Home3 (H1, H2 and H3)**

| Sampling area | $\Sigma_7$tri-hepta-BDEs | BDE-209 | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|
| H1R1F1 | 4.0 | 2.3 | 2.1 | 6.4 | 1.9 |
| H1R1F2 | 2.7 | 3.5 | 1.9 | 4.7 | 2.1 |
| H1R2F1 | 29.5 | 7.0 | 1.6 | 8.1 | 2.5 |
| H1R2F2 | 23.8 | 2.3 | 1.9 | 4.7 | 2.1 |
| H1R3F1 | 21.1 | 2.4 | 2.5 | 9.7 | 3.1 |
| H1R3F2 | 2.9 | 1.3 | 1.8 | 3.5 | 1.4 |
| H2R1F1 | 3.4 | 2.2 | 1.8 | 8.0 | 2.9 |
| H2R1F2 | 2.7 | 2.6 | 9.2 | 28.0 | 10.4 |
| H2R2F1 | 15.1 | 1.7 | 2.2 | 6.2 | 2.5 |
| H2R2F2 | 2.6 | 1.9 | 3.7 | 7.3 | 4.5 |
| H2R3F1 | 2.4 | 1.9 | 1.7 | 4.7 | 2.1 |
| H2R3F2 | 3.0 | 2.0 | 1.5 | 2.8 | 2.0 |
| H3R1F1 | 5.2 | 6.3 | 4.8 | 71.4 | 3.6 |
| H3R1F2 | 12.6 | 2.7 | 5.1 | 16.8 | 3.9 |
| H3R2F1 | 12.0 | 1.2 | 2.8 | 60.9 | 2.5 |
| H3R2F2 | 9.3 | 1.4 | 6.3 | 13.4 | 6.2 |
| H3R3F1 | 3.5 | 1.1 | 2.5 | 43.2 | 2.2 |
| H3R3F2 | 4.1 | 1.1 | 2.7 | 42.3 | 2.4 |

#### 4.3.2.2 Within-home temporal variation in concentrations of PBDEs and NBFRs in elevated surface dust.

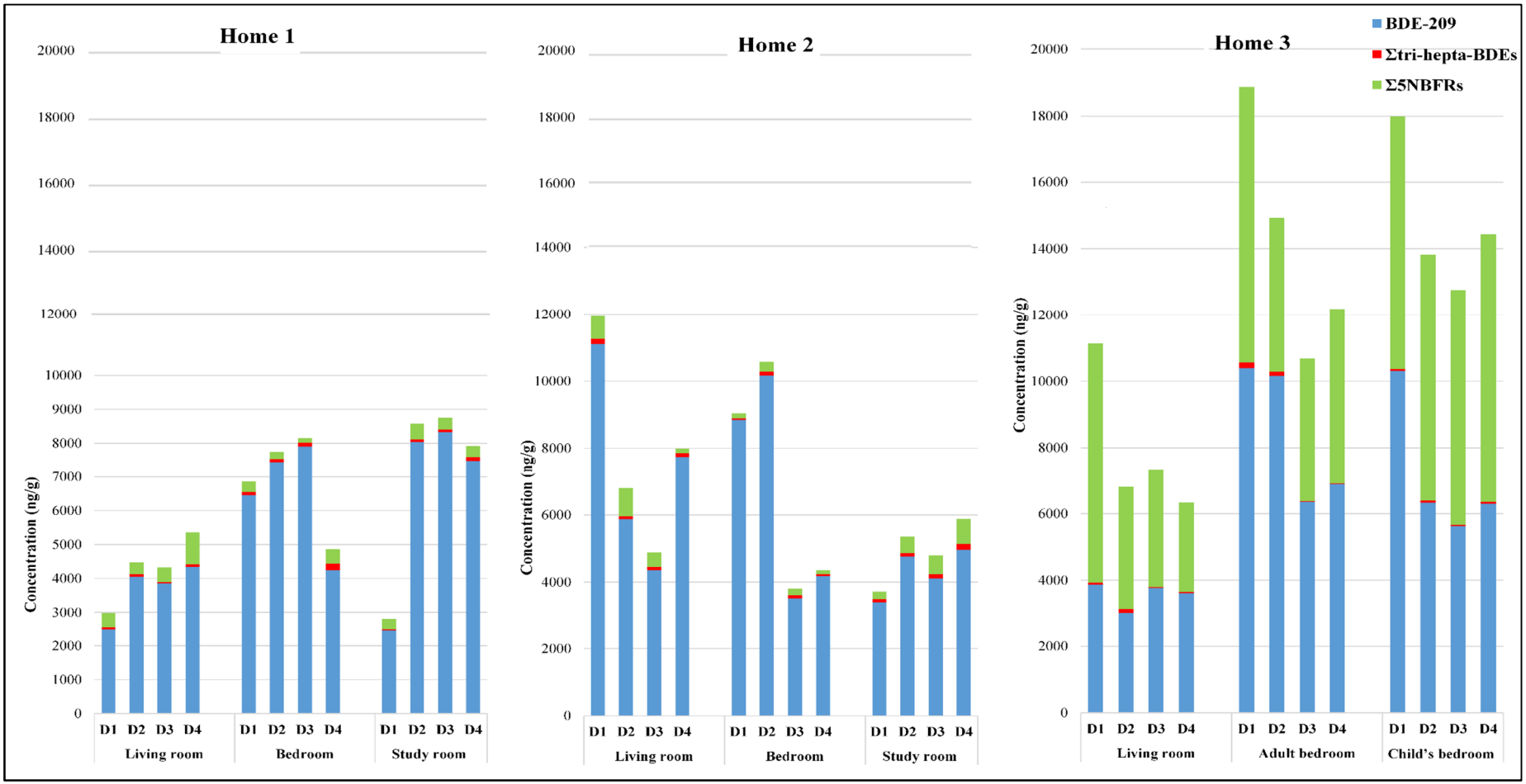
Within home temporal variation of PBDEs and $\Sigma_5$NBFRs was investigated in elevated surface dust from nine rooms within the three homes studied over four sampling periods. Figure 4.4 illustrates the observed within home temporal variation in concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209 and $\Sigma_5$NBFRs in indoor dust samples from elevated surfaces in the three investigated rooms in the three homes for the four sampling periods (D1-D4). Each sampling period at each home represented 2-3 months depending on the dust loading of the elevated

surfaces of each home. As shown in Tables 4.4, 4.8 and 4.12, substantial temporal variability was found in concentrations of PBDEs and NBFRs in elevated surface dust samples over the course of our sampling campaign. In Home 1, RSDs of BFR concentrations ranged from 13% for BEH-TEBP in the study to 117% for DBDPE in the bedroom. In Home 2, RSDs ranged from 16% for BDE-209 in the study to 103% for DBDPE in the same room. Meanwhile, in Home 3, RSDs ranged from 9% for BEH-TEBP in the child's bedroom to 91% for DBDPE in the living room. Our findings reveal DBDPE to display the highest RSD values in elevated surface dust. Generally, RSDs exceeded those obtained from replicate analysis of house dust reference material SRM2585 (Tables 2.11 and 2.12, Chapter 2). In addition, noticeable maximum: minimum ratios in BFR concentrations were found during the sampling period. However, these ratios (1.1- 31.6) are lower compared with those (1.1- 71.4) in floor dust samples. Table 4.14 lists maximum: minimum ratios of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and $\Sigma_5$NBFRs in elevated surface dust from the nine rooms studied during the sampling periods, along with Figure 4.4 illustrates temporal variation in concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209 and $\Sigma_5$NBFRs. To the best of the author's knowledge, this study is the first investigation of the temporal variability of BFRs in elevated surface dust.

**Table 4.14: Maximum: minimum ratio in concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in elevated surface dust samples (ES) from three rooms (R1, R2 and R3) in Home1, Home2 and Home3 (H1, H2 and H3)**

| Sampling area | $\Sigma_7$tri-hepta-BDEs | BDE-209 | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|
| H1R1ES | 2.1 | 1.8 | 3.8 | 2.1 | 2.7 |
| H1R2ES | 1.8 | 1.9 | 1.9 | 31.6 | 3.3 |
| H1R3ES | 4.2 | 3.4 | 1.4 | 3.5 | 1.4 |
| H2R1ES | 1.9 | 2.5 | 8.3 | 5.0 | 6.4 |
| H2R2ES | 2.4 | 2.9 | 2.1 | 6.9 | 2.4 |
| H2R3ES | 2.0 | 1.5 | 3.5 | 19.8 | 3.3 |
| H3R1ES | 4.1 | 1.3 | 2.7 | 4.3 | 2.7 |
| H3R2ES | 12.2 | 1.6 | 2.0 | 3.0 | 1.9 |
| H3R3ES | 1.8 | 1.8 | 1.2 | 10.3 | 1.1 |

**Figure 4.4: Within-home temporal variation in concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209 and $\Sigma_5$NBFRs in elevated surface dust samples in different rooms from three homes (H1, H2 and H3) over 3 sampling periods (D1= May+ Jun + Sep 13 for H1 and = May+ Jun 13 for H2 and H3, D2= Oct + Nov 13 for H1, = Sep+ Oct + Nov 13 for H2 and = Sep + Oct for H3, D3= Dec 13+ Jan 14 for H1 and H2, and = Nov 13 + Dec 13 for H3, and D4= Feb + March 14 for H1 and H2, and = Jan+ Feb +March for H3)**



### 4.3.3 Cause of temporal variability of BFR concentrations.

Temporal trends in concentrations of BFRs in a given room are likely affected by adding or removing potential emission sources. In Home 1, in the living room (H1R1), concentrations of BDE-209 in floor areas F1 and F2 increased in November 2013 compared with the previous and next samples (Figure 4.1) by factors of 1.8 and 2.0 for F1 area, and 2.1 and 3.5 for F2 area respectively. This is likely due to the small rug that was introduced to this room three weeks before the November sample was procured. After the November sampling date, the same rug was moved to the study (H1R3) causing an increase in the concentrations of BDE-209 levels in December 2013 and January 2014 samples by factors of 2.3 and 2.1 respectively. In the bedroom of the same home (H1R2), concentrations of $\Sigma_7$tri-hepta-BDEs and BDE-209 increased in dust samples from areas F1 and F2 taken in September 2013 compared to those taken in June 2013 by factors of 28 and 13 for $\Sigma_7$tri-hepta-BDEs, and 4.2 and 2.3 for BDE-209 for F1 and F2 areas respectively. Questionnaire data for this room, revealed that a new mattress was introduced after the June sample was taken, around 20 days before the September dust sample was taken. This mattress remained in the room for about 5 weeks before being removed prior to taking the October 2013 sample.

In Home 2, concentrations of BDE-209 in dust samples taken in September 2013 from the floor area F1 in the living room (H2R1) increased from those taken the previous month by a factor of 2.0. A possible explanation for this increase is that a piece of light fabric carpet was fitted over the main carpet in the living room 11 days before the September dust sample was obtained. This is reinforced by the sharp decline observed in concentrations of BDE-209 in subsequent dust samples, which coincides with the removal of the putative sources the week following collection of the September sample (Figure 4.2). Also in Home 2, concentrations of DBDPE in dust samples from floor areas F1 and F2 of the study (H2R3) were higher by factors of 4.7 and 1.8 in F1 and F2 respectively in the combined sample representing September, October, and November, compared to the concentrations present in the previously collected combined sample representing May and June. The reasons for this rise in DBDPE concentrations are unclear, since more than one change occurred in room contents between the two periods.

Interestingly, In Home 3, BDE-209 levels were stable in floor dust samples from the three investigated rooms with the exception of samples collected in October 2013. The

concentrations in that month increased sharply from those detected in September 2013 (Figure 4.3) in dust samples from the two floor areas F1 and F2 studied in the living room (H3R1) by factors of 6.3 and 2.4 in F1 and F2 respectively. Indeed, the floor dust sample from area F1 in this living room in October 2013, contained the highest concentration (19,800 ng/g) of BDE-209 detected in this study. The possible reason for increment in BDE-209 concentrations, may be the new rugs in F1 and F2 areas that were placed in this room around two weeks before the October sample was collected. As a result, October 2013 was the first time that these rugs had been vacuumed. Moreover, in the two bedrooms sampled in Home 3, DBDPE concentrations increased from October to November 2013 in dust collected from floor areas F1 and F2 by factors of 21.9 and 8.1 in the adult bedroom, and 40.7 and 26.5 in the child's bedroom for F1 and F2 respectively (Figure 4.3). While the increase in the adult bedroom may be attributed to the introduction of a new blanket, no obvious explanation exists for the increased DBDPE concentration in the child's bedroom.

Overall, our findings imply that temporal variation in concentrations of BFRs in floor dust is usually associated with changes in the room contents. However, it is noticeable that in Home 3, BEH-TEBP levels in the bedrooms declined gradually between May 2013 and November 2013, before stabilising in subsequent samples (Figure 4.3). Rather than a change in room contents, this decline might be the result of a gradual diminution in emissions of this NBFR as the room in question was furnished just prior to collection of the first sample.

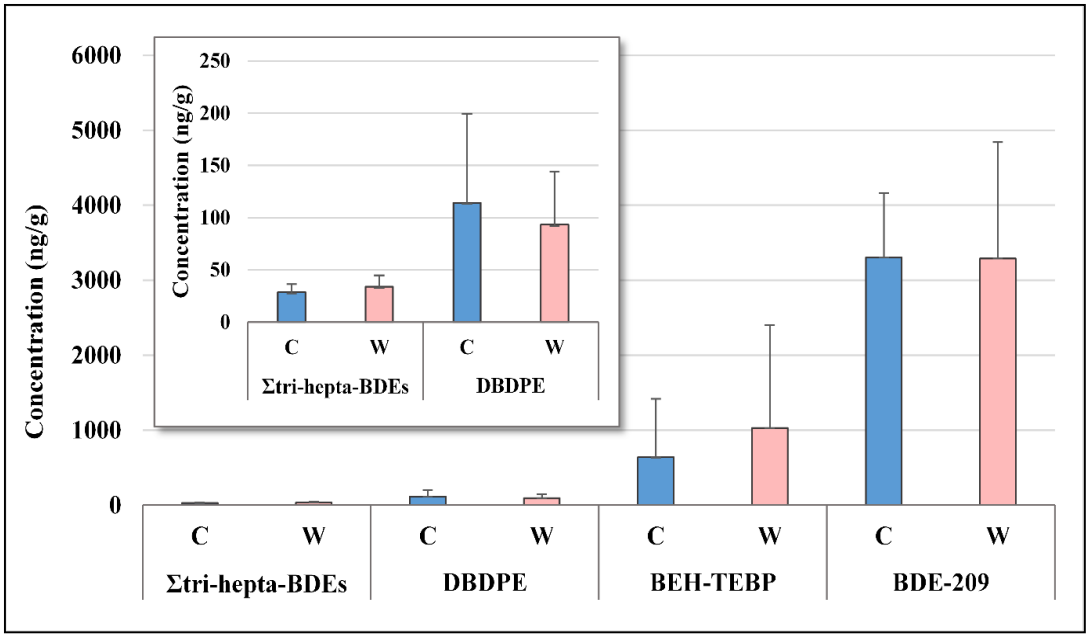
A few studies investigated within-room and within-home temporal variations in concentrations of BFRs in indoor dust. Our findings are consistent with those of a study by Harrad et al. (2008a), which suggested that most temporal variability was attributable to changes in room contents. Over a 9-10 month monitoring period, a substantial month-to-month rise in BDE-209 contamination of dust was found due to the fitting of a new fabric padded bed and polyester fabric blinds (Harrad et al., 2008a). In a similar vein, Muenhor and Harrad (2012) reported substantial within room temporal variability in ΣPBDE concentrations in monthly samples collected over an 8 month sampling period as a consequence of the introduction and removal of putative sources such as a TV and a bed. The study found RSDs for ΣPBDEs of between 15% and 200%. Meanwhile, another study (Allen et al., 2008) reported no significant difference between Penta- and Deca-BDE concentrations in house dust from living rooms and bedrooms in 20 homes collected 8 months apart. They attributed this

to minimal changes in room furnishings between the sampling periods (Allen et al., 2008). To the best of our knowledge, this study is the first to examine temporal variability in concentrations of NBFRs in indoor dust.

### 4.3.4 Seasonal variations in concentrations of PBDEs and NBFRs

Seasonal variations of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs concentrations were investigated in 136 floor dust samples and 36 elevated surface dust samples collected from 3 homes in the UK. Due to the sampling not being conducted over a full calendar year, May, June, September and October were deemed warmer months and November, December, January and February as colder months. Figure 4.5 illustrates average concentrations $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and DBDPE in warmer and colder seasons in floor dust samples.

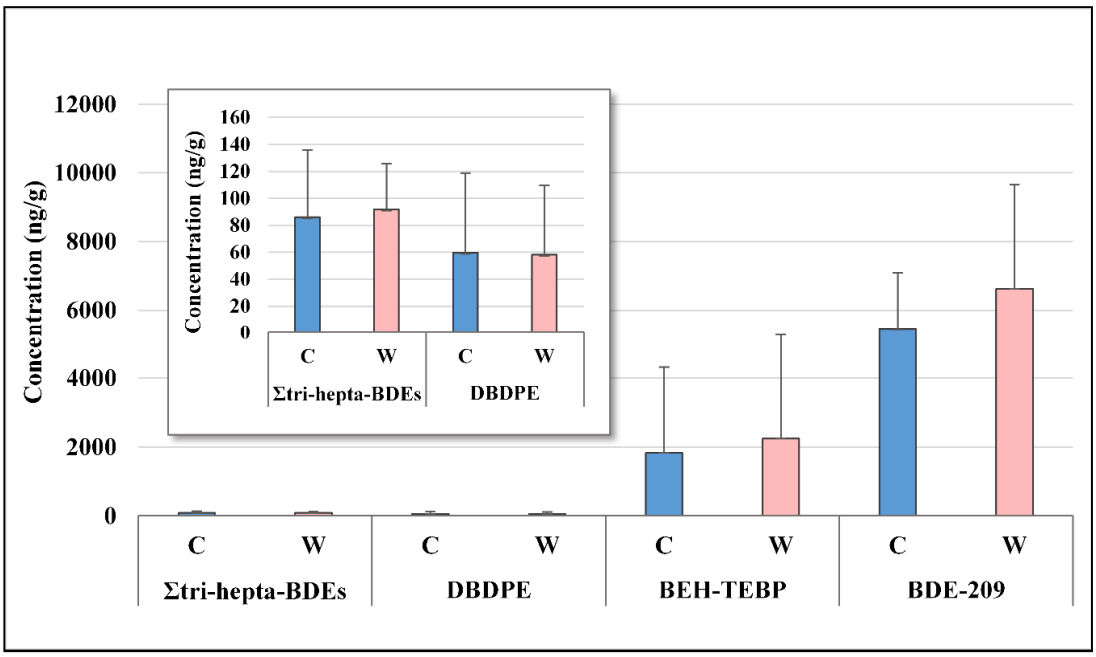
**Figure 4.5: Average concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and DBDPE in floor dust samples (n= 136) in warmer (W) and colder (C) seasons, with standard deviation (y error bar)**




The seasonal differences of the BFR concentrations in the elevated surface dust samples were investigated in indoor dust samples between colder and warmer periods. As monthly monitoring data were unavailable for elevated surface dust samples, the warm season was represented by the first four/five sampling months, while the cold season was represented by

the last months of the sampling period. Figure 4.6 illustrates the average concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and DBDPE in elevated surface dust samples (n=36) in colder and warmer seasons.

**Figure 4.6: Average concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs in elevated surface dust samples (n= 36) in warmer (W) and colder (C) periods, with standard deviation (y error bar)**




In each of the floor areas sampled (n =17), seasonal variability of $\Sigma_8$PBDEs (8 tri-deca-BDEs) and $\Sigma_5$NBFRs (PBEB, BTBPE, EH-TBB, BEH-TEBP and DBDPE) concentrations was investigated in the colder and warmer months. For the $\Sigma_8$PBDEs, average concentrations in 13 floor areas were higher in colder season than in a warmer, only in 4 areas, the average concentrations in the warmer season were higher and 3 of these 4 floor areas were found in the living rooms. In Home 1, the average concentrations of $\Sigma_8$PBDEs ranged between 1953 ng/g in R1F2 in the warmer season, and 3118 ng/g in R2F1 in the colder. In Home 2, $\Sigma_8$PBDE average concentrations ranged between 2391 ng/g in R3F1 in the warmer season and 3671 ng/g in R1F2 in the colder. In Home 3, $\Sigma_8$PBDEs average concentrations ranged between 3830 ng/g in R1F2 in the colder season and 7659 ng/g in R1F1 in the warmer. A t-test was applied to compare $\Sigma_8$PBDEs concentrations in each of the 17 sampling areas between colder and warmer seasons. With exception of two locations (H2R2F1 and H3R3F2), no significant

differences in $\Sigma_8$PBDEs were found between warmer and colder seasons in floor dust samples. $\Sigma_8$PBDE concentrations in colder season exceeded significantly those in the warmer, with *p* values of 0.002 and 0.046 in H2R2F1 and H3R3F2 respectively. Table 4.15 compares $\Sigma_8$PBDE average concentrations, standard deviation, and relative standard deviation, along with t-test *p* values between colder and warmer seasons in floor dust samples from the three rooms in the three homes studied.

In the three homes investigated, average concentrations of $\Sigma_5$NBFRs in 13 out of 17 floor areas were higher in the warmer season than in the colder, only in four locations (H1R1F2, H2R2F1, H1R2F1 and H2R3F1), the average concentrations were slightly higher in the colder season. In Home 1, Home 2 and Home 3, the average concentrations of $\Sigma_5$NBFRs ranged 109- 283, 218- 419 and 676- 4106 ng/g in H1, H2 and H3 respectively. The highest average concentrations in the warmer season were found in areas H1R2F1, H2R3F2 and H3R3F1 of H1, H2 and H3 respectively. T-test results revealed that $\Sigma_5$NBFR concentrations in four sampling areas in the warmer season exceeded significantly those in the colder in Homes 1 and 3, with *p* values of 0.046, 0.039, 0.051, and 0.023 in H1R1F2, H1R2F1, H3R2F1 and H3R3F1 respectively. Table 4.16 compares $\Sigma_5$NBFR average concentrations, standard deviation, and relative standard deviation, along with t-test *p* values between colder and warmer seasons in floor dust samples from the three rooms in the three homes studied.

**Table 4.15: Average concentrations (ng/g) and relative standard deviation (RSD) of $\Sigma_8$PBDEs (tri-deca-BDEs) in dust from two floor areas (F1 and F2) in different rooms (R1= living room, R2= bedroom, R3= study room, except for Home 2 Child`s bedroom) of Home 1, Home 2 and Home 3 along with variation in concentrations (t-test, p value) in warm (W) and cold (C) seasons**

| **Season** | **W** | **C** | **W** | **C** | **W** | **C** | **W** | **C** | **W** | **C** | **W** | **C** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Home** | **Home 1** | | | | **Home 2** | | | | **Home 3** | | | |
| **Location** | **R1F1** | | **R1F2** | | **R1F1** | | **R1F2** | | **R1F1** | | **R1F2** | |
| **Average** | 2229 | 2077 | 1953 | 2032 | 3287 | 3382 | 2480 | 3671 | 7659 | 4160 | 5109 | 3830 |
| **SD** | 373 | 820 | 706 | 1165 | 1241 | 630 | 667 | 759 | 8122 | 230 | 2591 | 376 |
| **RSD** | 17 | 40 | 36 | 57 | 38 | 19 | 27 | 21 | 106 | 6 | 51 | 10 |
| ***P* value** | 0.7566 | | 0.8609 | | 0.8871 | | 0.1043 | | 0.4527 | | 0.3449 | |
| **Location** | **R2F1** | | **R2F2** | | **R2F1** | | **R2F2** | | **R2F1** | | **R2F2** | |
| **Average** | 2681 | 3118 | 2746 | 2785 | 2408 | 2870 | 2489 | 3322 | 4284 | 4373 | 4071 | 4290 |
| **SD** | 1510 | 376 | 1019 | 378 | 324 | 386 | 582 | 488 | 204 | 169 | 576 | 185 |
| **RSD** | 56 | 12 | 37 | 14 | 13 | 13 | 23 | 15 | 5 | 4 | 14 | 4 |
| ***P* value** | 0.599 | | 0.955 | | 0.002 | | 0.213 | | 0.553 | | 0.398 | |
| **Location** | **R3F1** | | **R3F2*** | | **R3F1** | | **R3F2** | | **R3F1** | | **R3F2** | |
| **Average** | 2328 | 2378 | - | 2795 | 2391 | 2882 | 2644 | 3165 | 4431 | 4591 | 4237 | 4598 |
| **SD** | 366 | 1091 | - | 345 | 387 | 473 | 540 | 687 | 188 | 164 | 36 | 209 |
| **RSD** | 16 | 46 | - | 12 | 16 | 16 | 20 | 22 | 4 | 4 | 1 | 5 |
| **P value** | 0.942 | | - | | 0.252 | | 0.261 | | 0.334 | | 0.046 | |

* This location was not available for sampling in the first five months

**Table 4.16: Average concentrations (ng/g), standard deviation (SD) and relative standard deviation (RSD) of $\Sigma_5$NBFRs in dust from two floor areas (F1 and F2) in different rooms (R1= living room, R2= bedroom, R3= study room, except for Home 2 Child`s bedroom) of Home 1, Home 2 and Home 3, along with variation in concentrations (T-test p value) in warm (W) and cold (C) seasons**

| **Season** | **W** | **C** | **W** | **C** | **W** | **C** | **W** | **C** | **W** | **C** | **W** | **C** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Home | **Home 1** | | | | **Home 2** | | | | **Home 3** | | | |
| Location | **R1F1** | | **R1F2** | | **R1F1** | | **R1F2** | | **R1F1** | | **R1F2** | |
| Average | 169 | 144 | 168 | 109 | 302 | 251 | 220 | 245 | 1721 | 1516 | 1360 | 676 |
| SD | 31 | 34 | 33 | 14 | 122 | 103 | 59 | 162 | 263 | 753 | 367 | 211 |
| RSD | 18 | 23 | 20 | 12 | 40 | 41 | 27 | 66 | 15 | 50 | 27 | 31 |
| *P* value | 0.204 | | 0.046 | | 0.366 | | 0.709 | | 0.701 | | 0.071 | |
| Location | **R2F1** | | **R2F2** | | **R2F1** | | **R2F2** | | **R2F1** | | **R2F2** | |
| Average | 283 | 160 | 191 | 137 | 218 | 268 | 282 | 247 | 3308 | 2149 | 3393 | 1947 |
| SD | 64 | 16 | 37 | 34 | 85 | 49 | 133 | 103 | 835 | 148 | 1060 | 201 |
| RSD | 23 | 10 | 19 | 25 | 39 | 18 | 47 | 42 | 25 | 7 | 31 | 10 |
| *P* value | 0.039 | | 0.142 | | 0.416 | | 0.583 | | 0.051 | | 0.071 | |
| Location | **R3F1** | | **R3F2*** | | **R3F1** | | **R3F2** | | **R3F1** | | **R3F2** | |
| Average | 215 | 222 | - | 113 | 241 | 292 | 419 | 409 | 4106 | 2442 | 3895 | 2488 |
| SD | 64 | 107 | - | 15 | 52 | 93 | 99 | 132 | 564 | 268 | 739 | 548 |
| RSD | 30 | 48 | - | 13 | 22 | 32 | 24 | 32 | 14 | 11 | 19 | 22 |
| P value | 0.932 | | - | | 0.487 | | 0.937 | | 0.023 | | 0.070 | |

* This location was not available for sampling in the first five months

### 4.3.5 Cause of seasonal variability of BFR concentrations.

As BFRs are semi volatile organic compounds, their emission from consumer products would be expected to increase during the warm seasons. This hypothesis was examined by Hazrati and Harrad (2006) who found that airborne levels of Σtri-hexa-BDEs in warmer months were generally higher than those in colder months, although seasonal variability in indoor air levels was less significant than for outdoor air (Hazrati and Harrad 2006). This is consistent with the volatilisation-adsorption mechanism of BFR transfer from tconsumer products into indoor dust, which is a likely explanation for low brominated BFRs. However, this mechanism is likely not appropriate to explain the behaviour of more highly brominated BFRs such as BDE-209 and DBDPE. Abrasion of particles or fibres from treated products and direct contact with indoor dust, which are less affected by the temperature, is a more likely mechanism via which more highly brominated compounds undergo source-to-dust transfer (Suzuki et al., 2009; Webster et al., 2009; Harrad et al., 2010b; Rauert et al., (2014a). Our finding revealed that, despite the absence of significant seasonal variation in PBDE concentrations (in only 2 out of 17 floor areas), average concentrations in 13 out of 17 floor areas were higher in colder seasons than in warmer. This indicates that the seasonal trend of ΣPBDEs is driven largely by BDE-209 behaviour, as the percentage contribution to ΣPBDEs is more than 90% of $\Sigma_8$PBDEs in dust samples (Section 3.3, Chapter 3). In contrast, the seasonal trend of $\Sigma_5$NBFRs is driven predominantly by BEH-TEBP as this is the main contributor to $\Sigma_5$NBFRs with contributions of 52- 94% compared with DBDPE which has corresponding mean percentage contributions of 3- 42% (Section 3.3, Chapter 3). In addition, despite the low reported vapour pressure of BEH-TEBP, our findings in Chapter 5 suggest that BEH-TEBP behaves similarly to lower brominated compounds.

The findings of this study are consistent with previous studies that have investigated seasonal variation in BFR concentrations indoors. Batterman et al. (2009) monitored 12 US houses and garages in summer and spring, reporting limited consistency between PBDE concentrations in indoor dust collected in the two seasons. Muenhor and Harrad, (2012) investigated Σtri-hexa-BDEs in 14 sampling areas in UK homes over an 8 month period. Despite the absence of significant seasonal variation, average ΣPBDEs concentrations in floor dust from 7 of 14 sampling areas were higher in colder months (September to March) than in warmer months (March to September), while in the other 7 sampling areas, average ΣPBDE concentrations in warmer months were higher than those in colder months. This is the only study that has

specifically addressed this subject. Its authors suggested that any increase in PBDE emission during the warmer months, will be offset by increased partitioning of PBDEs to the air rather than dust. Moreover, greater volatilisation emissions from sources in warmer months, will likely be offset by increased ventilation. (Muenhor and Harrad 2012). Yu et al. (2012) reported that the average concentrations of PBDEs in house dust samples from floors and other surfaces were ranked as summer > winter > spring > autumn. In addition, this study pointed out that the seasonal variations among the spring, summer, and winter samples were not statistically significant, while concentrations in the autumn samples were significantly lower than those in other seasons for both in- and out-house dust (Yu et al. 2012). However, there are many possible factors that influence seasonal variability of BFRs such as: presence of emission sources, differences in indoor temperature between the different seasons; BFR physicochemical properties, the mechanism of transfer from potential emission source to dust (e.g. abrasion of source materials and indoor dust and ventilation system, and the people lifestyle.

## 4.4 Temporal and seasonal variability impacts on PBDE and NBFR human exposure assessments

As presented in Tables 4.1- 4.12 and Figures 4.1-4.4, considerable temporal variations in concentrations of some BFRs were found in dust sampled in three UK houses over a nine month period, particularly for $\Sigma_7$tri-hepta-BDEs and DBDPE. In addition, appreciable maximum: minimum ratios are represented in tables 4.13 and 4.14. To evaluate to what extent BFR temporal variation may affect human exposure assessment, we compared the RSD values for selected BFRs. We also examined the extremes of exposure assessment using the ratio between the highest and lowest concentrations for a given room.

In Home 1, the highest RSD values of $\Sigma_7$tri-hepta-BDEs were 92%, 86% and 123%, which appeared in H1R2F1, H1R2F2 and H1R3F1 respectively. This implies that human exposure to $\Sigma_7$tri-hepta-BDEs in these areas would vary to the same extent. In addition, in these floor areas, $\Sigma_7$tri-hepta-BDE maximum: minimum ratios were 30, 24, and 21 respectively, implying that exposure assessments could be underestimated or overestimated by factors of 30, 24, and 21 if by chance one sample was taken from these areas in the month recording the lowest concentration as opposed to the month when the highest concentration was recorded. The highest RSD value of BEH-TEBP (73%) was found in H1R1ES with the highest maximum:

minimum ratio of 9.2 in H2R1F2. Moreover, considerable temporal variations in concentrations of DBDPE were found in the three homes studied, particularly in Home 3. The RSD values of DBDPE in H3R2F2 and H3R3F2 were the highest among all BFRs RSD values, with values of 138% and 159% respectively. The highest maximum: minimum ratio was 71 which appeared in H3R1F1.

As presented in Tables 4.15 and 4.16, seasonal variability in concentrations of $\Sigma_8$PBDE and $\Sigma_5$NBFR were found in some floor areas. The highest RSD value (106%) was found in $\Sigma_8$PBDE concentrations in the warmer season, while the highest RSD value of $\Sigma_5$NBFR (66%) was found in H2R1F2 in the colder.

These considerable temporal and seasonal variability indicate the uncertainty associated with basing exposure assessments via dust ingestion for BFRs based on a single grab sample taken from a given area at a given point in time. Of course, such variability will be masked to an unknown extent when the exposure assessment is based on dust samples taken at a similar time, but in multiple rooms/homes etc.

## 4.5 Conclusion

This chapter investigates within-room and within-home temporal variations and seasonal variations in concentrations of PBDEs and NBFRs in floor dust and elevated surface dust from 3 homes in the UK. Our findings reveal substantial variability in the concentrations of some BFRs during the sampling period. Temporal variations in BFR levels appear affected by the addition or removal of a potential emission source. For PBDEs, variations in $\Sigma_7$tri-hepta-BDEs concentrations were associated with the presence/absence of electronic devices and old foam furniture, while variations in concentrations of BDE-209 were associated with fabric materials and carpets. For NBFRs, BEH-TEBP variability was strongly associated with new bedroom furnishings, while DBDPE temporal variability was not associated with any particular source(s). Temporal variations in most of our target compounds were found mainly to be “step” changes; however, concentrations of BEH-TEBP gradually declined, which might naturally occur as a result of gradual attainment of equilibrium between the gas phase and particulate phase in indoor air.

Seasonal variations in BFR concentrations revealed that, with the exception of DBDPE, in general, average concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209 and BEH-TEBP in elevated surfaces dust samples were higher in warmer seasonss than in colder, while in floor dust, BDE-209 average concentrations was comparable in both colder and warmer seasons. For individual areas, average concentrations of $\Sigma_8$tri-deca-BDEs in floor dust in colder season were higher than those in warmer in living rooms (H1R1F1, H3R1F1 and H3R1F2). In contrast, average concentrations $\Sigma_5$NBFRs in the majority of floor areas in warmer seasons were higher than colder. In general, concentrations of $\Sigma_7$tri-hepta-BDEs and BEH-TEBP tend to be higher in warmer seasons than BDE-209 and DBDPE.

Substantial temporal and seasonal variation has implications for human exposure assessments particularly for $\Sigma_7$tri-hepta-BDEs and DBDPE due to the high RSD and maximum: minimum ratio values reported for these parameters here. Our data provide a measure of the uncertainty associated with assessments of human exposure to PBDEs and NBFRs via dust ingestion that are based on samples taken from a given room area and a given point in time.

# CHAPTER 5

## DISTRIBUTION PATTERN OF LEGACY AND "NOVEL" BROMINATED FLAME RETARDANTS IN DIFFERENT PARTICLE SIZE FRACTIONS OF INDOOR DUST

This chapter contains sections of text taken verbatim from the following publication: "L. S. Al-Omran, S. Harrad. "Distribution pattern of legacy and "novel" brominated flame retardants in different particle size fractions of indoor dust in Birmingham, United Kingdom", *Chemosphere*, 157, 124-131 (2016)".

## 5.1 Summary

This chapter reports on the particle size distribution of PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209) and NBFRs (PBEB, EH-TBB, BEH-TEBP, BTBPE and DBDPE) in indoor dust, from Birmingham, UK. Five paired samples of floor dust and elevated surface dust were fractionated into three different particle size fractions, large size P1 (125-250 μm), medium size P2 (63-125 μm), and fine size P3 (25-63 μm). Concentrations of target BFRs were determined in each of these fractions as well as in bulk dust BD (< 250 μm) to test the following hypotheses: (a) BFR concentrations will increase with decreasing particle size, (b) BFR concentrations in elevated surface dust will exceed those in floor dust, (c) variations in dust organic carbon content cannot account for any variations in BFR concentrations between different particle size fractions, and (d) selection of dust particle size fraction is an important factor for human exposure assessment.

The findings of this study showed that BDE-209 was the predominant compound, with average concentrations ranging between 2675 ng/g in the finest particle size fraction (P3) to 3207 ng/g in the largest particle size fraction (P1). The next most abundant BFR was BEH-TEBP, for which concentrations ranged between 671 ng/g in P1 to 1265 ng/g in P3, followed by DBDPE for which concentrations ranged between 165 ng/g in P2 to 210 ng/g in P3. Concentrations of other individual target contaminants ranged between < 0.1 to 40.9 ng/g. Concentrations of $\Sigma_7$tri-hepta-BDEs (ΣBDE-28, BDE-100, BDE-47, BDE-99, BDE-153, BDE-154 and BDE-183) fell between 48.1 ng/g in P1 to 86.9 ng/g in P3.

With respect to the mass distribution of particles within bulk dust (<250 μm); on average, 46.6% w/w of bulk dust was associated with P3 (25-63 μm), 32.7% w/w with P2 (63-125 μm) and 20.6% w/w with P1 (125-250 μm).

One way repeated measures ANOVA tests and t-tests were applied to compare means of BFR concentrations between different particle size fractions and between elevated surface dust and floor dust respectively. The ANOVA test revealed significant differences between concentrations of some BFRs between different particle size fractions. Specifically, concentrations of more volatile BFRs (i.e. $\Sigma_7$tri-hepta-BDEs) in the finest particles (P3) exceeded significantly ($p < 0.05$) those in BD, P2 and P1, with those in P2 exceeded significantly in BD and P1. In contrast, no significant differences were found between concentrations in different particle size fractions for less volatile BFRs, specifically: BDE-209, EH-TBB, BTBPE and DBDPE. However, t-test analysis observed that with the exception of DBDPE, concentrations of BFRs in elevated surface dust exceeded significantly those in floor dust ($p < 0.002$) in BD, P1, P2 and P3.

We found a significant positive linear correlation between BFR concentrations in all samples and their corresponding total organic carbon (TOC) content. Given this affinity of BFRs for organic matter, variations in organic carbon content between different particle size fractions and between ESD and FD could potentially influence BFR concentrations. However, there was no significant difference in this study (only in one case, P1 exceeded significantly those in BD with a *p* value of 0.027) between TOC values measured in different particle size fractions with average values of 33.2%, 33.5%, 35.1% and 33.6% detected in BD, P1, P2 and P3 respectively. This indicates that differences in the organic carbon content of dust cannot explain the higher concentrations of some BFRs in finer dust particles, nor the higher concentrations present in elevated surface compared to floor dust. Instead, we suggest that such variations in concentrations with particle size of more volatile BFRs are more likely attributable to particle size-related variations in particle surface area to volume ratios, that are greater in finer particles. While this is the dominant influence for more volatile BFRs, for which the principal BFR source to dust is atmospheric deposition; we suggest it is less important for higher molecular weight BFRs, for which additional pathways are also influential. These pathways (abrasion of sources and transfer via direct dust-source contact)

are less dependent on particle size, consistent with the absence of significant variation in concentrations of less volatile BFRs with particle size.

Given our findings, we suggest that for human exposure assessment, particle size selection is an important consideration. To illustrate, we used our concentration data to derive separate estimates of exposure via dust ingestion based on ingestion of the size fractions 25-63 μm and 25-250 μm respectively. This revealed that for our high-end exposure estimates, estimates based on ingestion of the 25-63 μm size fraction were 1.54, 0.86, 1.75 and 1.27 times those based on ingestion of the 25-250 μm size fraction, for $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and DBDPE respectively.

## 5.2 Sampling and sample preparation

Between September 2013 and February 2014, indoor dust samples (46) were collected from the living room and two bedrooms in each of 5 homes in Birmingham, UK. Elevated surface dust (ESD) and floor dust (FD) were collected every month for 4 months in two homes, and for 5 months in three. In order to provide sufficient dust mass for fractionation (especially necessary for ESD for which dust mass loadings in these UK homes were very low), the ESD and FD samples from each home were then combined to yield two raw dust samples (one ESD and one FD) from each of the 5 homes, yielding a total of 10 samples. Samples were collected according to a clearly defined standard protocol (Chapter 2, section 2.3). Information on potential influences on BFR contamination such as: number and type of putative sources like electronic devices, foam-filled furniture and floor material, ventilation system, house cleaning method was recorded on the questionnaire shown in Appendix 1.

Initially, to obtain bulk dust samples (referred to here as BD), all samples were sieved using a pre-cleaned, n-hexane rinsed 250 μm mesh stainless testing sieve, covered with the lid and shaken for 3-5 min. After weighing, BD samples were fractionated into three different particle size fractions, 125-250 μm (referred to as large particle size - P1), 63-125 μm (referred to as medium particle size - P2) and 25-63 μm (referred to as fine particle size – P3). Fractionation was achieved by using 63 μm, 125 μm, and 250 μm stainless sieves which were placed over each other and shaken by hand for 5-7 min. Following fractionation, the mass of each fraction was recorded.

## 5.3 Results and discussion

In all dust samples analysed (n = 40), concentrations of BDE-28, BDE-100, BDE-154, and PBEB were very low, and they are thus excluded from statistical analysis for individual comparison. However, they were included in calculation of $\Sigma_7$tri-hepta-BDEs and $\Sigma_5$NBFRs. $\Sigma_7$tri-hepta-BDEs refers to the summation of seven congeners (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, and BDE-183), $\Sigma_5$NBFRs represent the sum of PBEB, EH-TBB, BTBPE, BEH-TEBP, and DBDPE, with ΣBFRs equalling the sum of $\Sigma_7$tri-hepta-BDEs, BDE-209 and $\Sigma_5$NBFRs.

### 5.3.1 Relationship between BFRs in different particle sizes

In all dust samples, BDE-47, BDE-99, BDE-153, BDE-209, BEH-TEBP, and DBDPE were found at detection frequencies of 100 %, while BDE-28, BDE-100, BDE-154, BDE-183, PBEB, EH-TBB and BTBPE were found at detection frequencies of 48%, 50%, 78%, 93%, 63%, 95% and 90% respectively. BDE-209 was the predominant congener making average percentage contributions to ΣBFRs of 74.3%, 77.3%, 69.2%, and 62.7% in BD, P1, P2 and P3 dust samples respectively. $\Sigma_5$NBFRs contributed 24.2%, 21.5%, 29.1% and 35.3% ΣBFRs, while $\Sigma_7$tri-hepta-BDEs represented 1.5 %, 1.2 %, 1.7 %, and 2.0 % of ΣBFRs. Of the target NBFRs, BEH-TEBP predominated, with corresponding mean percentage contributions to $\Sigma_5$NBFRs of 76.9%, 75.1%, 83.1%, and 83.9%, followed by DBDPE with percentages 20.1 %, 21.9 %, 14.1 % and 13.9 % in BD, P1, P2 and P3 dust samples respectively. EH-TBB and BTBPE were the least abundant of the target NBFRs, with EH-TBB comprising 0.95 %, 1.08 %, and 1.05 % and 0.79% $\Sigma_5$NBFRs, and BTBPE 1.94%, 1.74%, 1.64% and 1.24% $\Sigma_5$NBFRs in BD, P1, P2 and P3 respectively. Figure 5.1 compares average concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, and $\Sigma_5$NBFRs, while Figure 5.2 shows concentrations and profiles of 7 individual tri-hepta-BDEs and 5 NBFRs in BD, P1, P2 and P3.

**Figure 5.1: Average concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209 and $\Sigma_5$NBFRs in three particle sizes fractions (P1=125-250 µm, P2=63-125 µm, P3=25-63 µm) and Bulk dust (BD)**

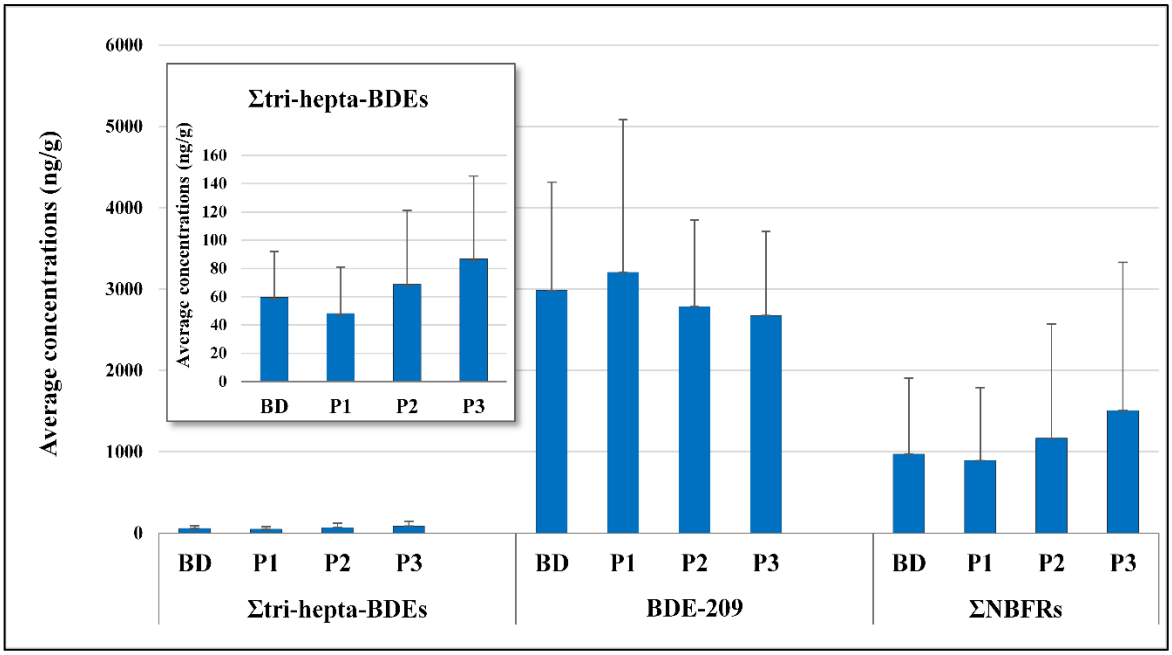
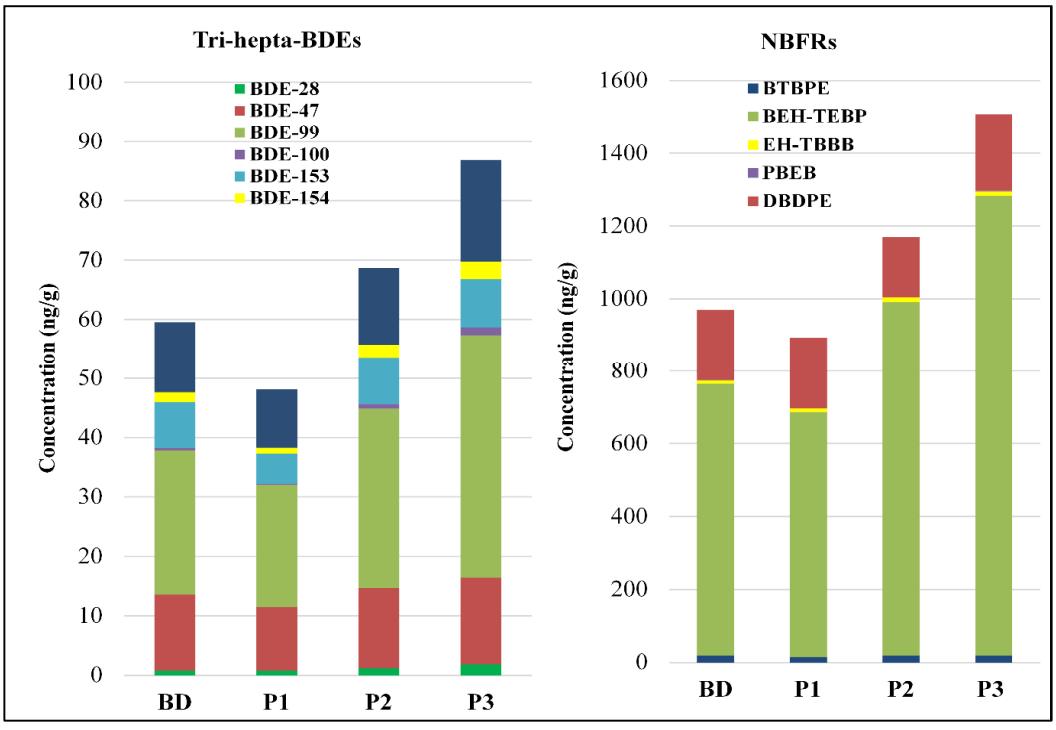
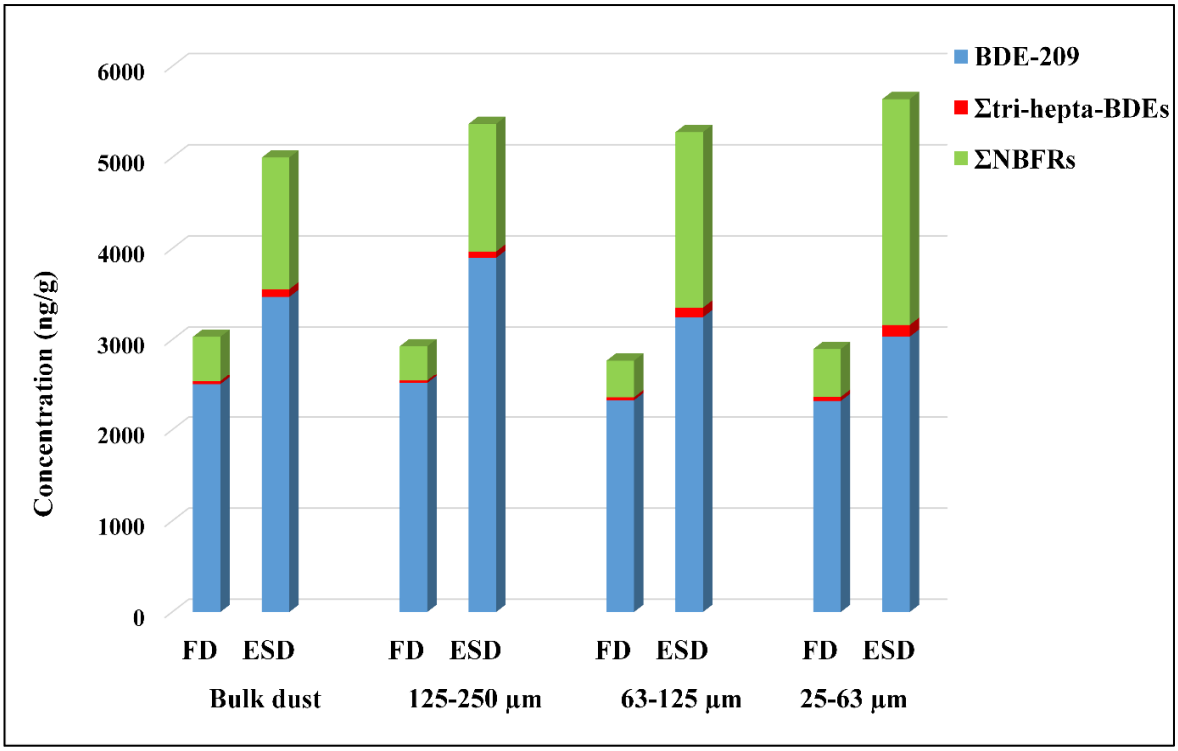



**Figure 5.2: Concentrations and profiles of tri-hepta-BDEs and NBFRs in BD (bulk dust), P1 (125 - 250 µm), P2 (63 - 125 µm) and P3 (25 - 63 µm)**



Following log transformation of concentrations expressed on a dry dust weight basis, a paired t-test was applied to test the hypothesis that concentrations of our target BFRs in ESD would exceed significantly those in FD. As hypothesised and consistent with our study of Iraqi dust samples (Chapter 7), the t-test analysis revealed that with the exception of DBDPE ($p$ = 0.978), our target compounds in elevated surface dust exceeded significantly those in floor dust with $p$ values < 0.002 in BD, P1, P2 and P3. Average concentrations in ESD exceeded those in FD by the following factors: for $\Sigma_7$tri-hepta-BDEs, 2.4, 2.5, 3.2 and 2.9, for BDE-209, 1.4, 1.6, 1.4, and 1.3, and for $\Sigma_5$NBFRs, 2.9, 3.6, 4.7 and 4.6 in BD, P1, P2 and P3 respectively. Figure 5.3 illustrates arithmetic mean concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209 and $\Sigma_5$NBFRs in the three particle size fractions and bulk dust for both floor and elevated surface dust samples.

**Figure 5.3: Comparison of mean concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209 and $\Sigma_5$NBFRs in three particle sizes and bulk dust of both floor dust (FD) and elevated surface dust (ESD)**



### 5.3.2 Concentrations of PBDEs and NBFRs in different particle sizes

In all dust samples, concentrations of individual contaminants varied between different particle size fractions. The highest mean concentrations of BDE-47, BDE-99, BDE-153 and BDE-183 were found in the finest particle size fraction (P3) with values of 14.5, 40.9, 8.1 and 17.2 ng/g respectively, while the highest mean concentration of BDE-209 (3207 ng/g) was found in the largest particle size fraction (P1). For NBFRs, the highest mean concentrations of EH-TBB and BTBPE were found in P2 with values of 12.2 and 19.2 ng/g respectively, while the highest mean concentrations of BEH-TEBP and DBDP were found in P3 with values of 1265 and 210 ng/g respectively. Tables 5.1 and 5.2 provide mean, median, minimum, maximum concentrations and detection frequencies of PBDEs and NBFRs in bulk dust (BD) and the three particle size fractions (P1, P2, and P3).

**Table 5.1: Statistical summary of concentrations (ng/g) of target PBDEs in three particle size fractions (P1= 125-250 µm, P2= 63-125 µm and P3= 25-63 µm) and Bulk Dust (BD)**

| Concentration | Fraction | BDE-28 | BDE-47 | BDE-99 | BDE-100 | BDE-153 | BDE-154 | BDE-183 | $\Sigma_7$tri-hepta-BDEs | BDE-209 |
|---|---|---|---|---|---|---|---|---|---|---|
| Mean | BD | 0.9 | 12.7 | 24.2 | 0.5 | 7.7 | 1.7 | 11.9 | 59.5 | 2986 |
| | P1 | 0.8 | 10.7 | 20.5 | 0.2 | 5.1 | 1.0 | 9.8 | 48.1 | 3207 |
| | P2 | 1.2 | 13.5 | 30.2 | 0.8 | 7.9 | 2.2 | 12.9 | 68.7 | 2786 |
| | P3 | 1.9 | 14.5 | 40.9 | 1.3 | 8.1 | 3.0 | 17.2 | 86.9 | 2675 |
| Median | BD | 0.7 | 11.5 | 20.4 | < 0.1 | 7.1 | 0.7 | 10.3 | 53.2 | 2655 |
| | P1 | 0.5 | 9.7 | 14.4 | < 0.1 | 4.9 | 0.5 | 9.9 | 40.2 | 2749 |
| | P2 | 0.8 | 11.1 | 16.1 | 0.6 | 6.0 | 0.9 | 7.8 | 56.9 | 2654 |
| | P3 | 1.2 | 13.2 | 26.9 | 1.2 | 5.6 | 1.6 | 8.3 | 72.2 | 2765 |
| Min | BD | < 0.1 | 2.6 | 3.3 | < 0.1 | 0.3 | < 0.2 | < 0.2 | 18.2 | 1637 |
| | P1 | < 0.1 | 0.6 | 0.5 | < 0.1 | 0.3 | < 0.2 | < 0.2 | 10.5 | 1485 |
| | P2 | < 0.1 | 1.0 | 1.1 | < 0.1 | 0.4 | < 0.2 | 0.4 | 11.7 | 1196 |
| | P3 | < 0.1 | 2.1 | 5.3 | < 0.1 | 1.3 | < 0.2 | 0.8 | 19.3 | 1086 |
| Max | BD | 3.0 | 30.8 | 57.0 | 1.6 | 16.1 | 6.6 | 32.7 | 116.4 | 6279 |
| | P1 | 2.1 | 26.8 | 63.9 | 0.8 | 9.1 | 4.0 | 24.6 | 119.6 | 8114 |
| | P2 | 4.6 | 29.9 | 86.9 | 2.5 | 16.9 | 6.9 | 36.5 | 166.9 | 4308 |
| | P3 | 7.3 | 37.8 | 96.8 | 3.0 | 19.0 | 8.9 | 59.9 | 199.5 | 4035 |
| Detection% | All samples | 48 | 100 | 100 | 50 | 100 | 78 | 93 | 100 | 100 |

$\Sigma_7$tri-hepta-BDEs BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, and BDE-1

**Table 5.2: Statistical summary of concentrations (ng/g) of target NBFRs in three particle size fractions (P1= 125-250 µm, P2= 63-125 µm and P3= 25-63 µm) and Bulk Dust (BD)**

| Concentration | Fraction | PBEB | EH-TBB | BTBPE | BEH-TEBP | DBDPE | $\Sigma_5$NBFRs |
|---|---|---|---|---|---|---|---|
| Mean | BD | 1.54 | 9.2 | 18.8 | 746 | 195 | 970 |
| | P1 | 0.78 | 9.6 | 15.5 | 671 | 196 | 893 |
| | P2 | 1.30 | 12.2 | 19.2 | 972 | 165 | 1169 |
| | P3 | 1.54 | 11.9 | 18.7 | 1265 | 210 | 1507 |
| Median | BD | 1.07 | 5.8 | 15.0 | 320 | 157 | 563 |
| | P1 | 0.74 | 6.4 | 16.7 | 220 | 112 | 595 |
| | P2 | 0.93 | 8.0 | 11.4 | 333 | 56 | 622 |
| | P3 | 1.32 | 7.8 | 13.3 | 355 | 111 | 703 |
| Min | BD | < 0.1 | 4.0 | < 2.8 | 80 | 11.4 | 300 |
| | P1 | < 0.1 | 1.8 | < 2.8 | 73 | 22.0 | 164 |
| | P2 | < 0.1 | 2.5 | < 2.8 | 79 | 8.1 | 221 |
| | P3 | < 0.1 | < 0.5 | < 2.8 | 94 | 6.6 | 314 |
| Max | BD | 4.74 | 22.9 | 61.2 | 3187 | 700 | 3306 |
| | P1 | 2.27 | 25.2 | 52.9 | 2659 | 899 | 2962 |
| | P2 | 3.36 | 44.0 | 87.9 | 4359 | 736 | 4521 |
| | P3 | 3.85 | 36.1 | 50.8 | 5519 | 1004 | 5601 |
| Detection% | All samples | 63 | 95 | 90 | 100 | 100 | 100 |

$\Sigma_5$NBFRs PBEB, EH-TBB, BTBPE, BEH-TEBP and DBDPE

BFRs were not consistently distributed between dust samples from the five homes examined in this study. Among the five homes, $\Sigma_7$tri-hepta-BDEs and BDE-209 concentrations in Home 1 were the highest, while NBFRs in Home 1 were present at lower levels comparable with those in the other homes studied. Home 2 and Home 3 contained the highest concentrations of EH-TBB, BTBPE and BEH-TEBP, while Home 4 displayed the highest DBDPE levels. This may be attributed to the older furnishings present in Home 1, in contrast to the newer furnishings of Home 2 and new carpet in Home 3. Figures 5.4, 5.5, 5.6 and 5.7 illustrate $\Sigma_7$tri-

hepta-BDEs, BDE-209, BEH-TEBP and DBDPE levels in the five homes studied in both elevated surface dust and floor dust samples.

**Figure 5.4: $\Sigma_7$tri-hepta-BDEs concentrations in different particle size fractions of elevated surface dust (ESD) and floor dust (FD) samples from five homes**

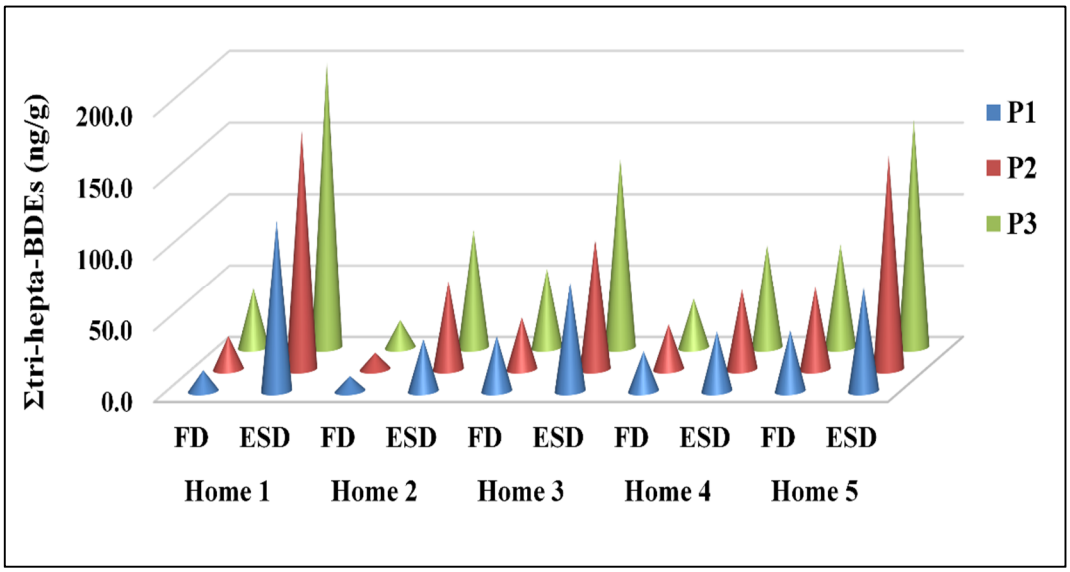



**Figure 5.5: BDE-209 concentrations in different particle size fractions of elevated surface dust (ESD) and floor dust (FD) samples from five homes**

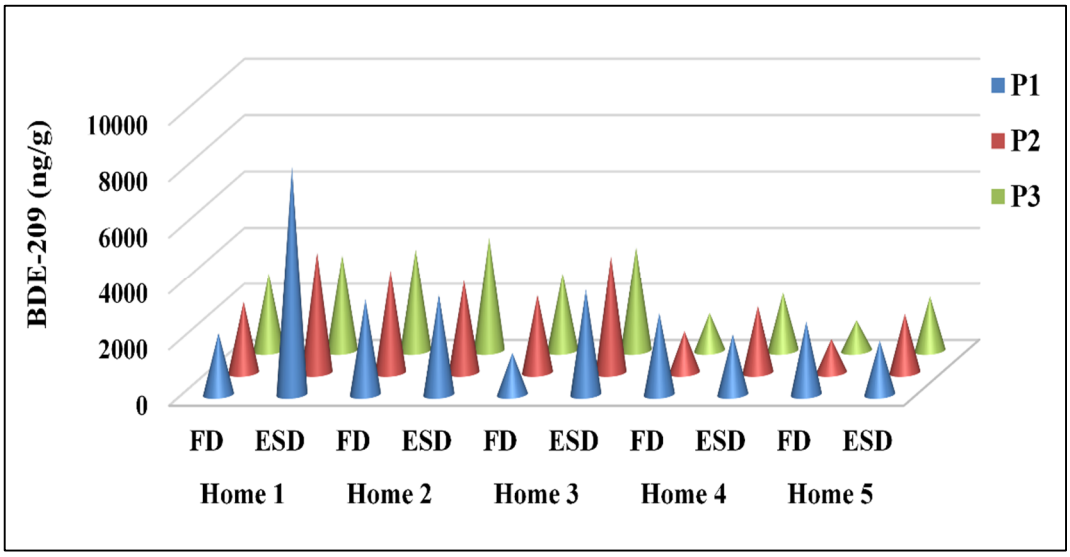


**Figure 5.6: BEH-TEBP concentrations in different particle size fractions of elevated surface dust (ESD) and floor dust (FD) samples from five homes**

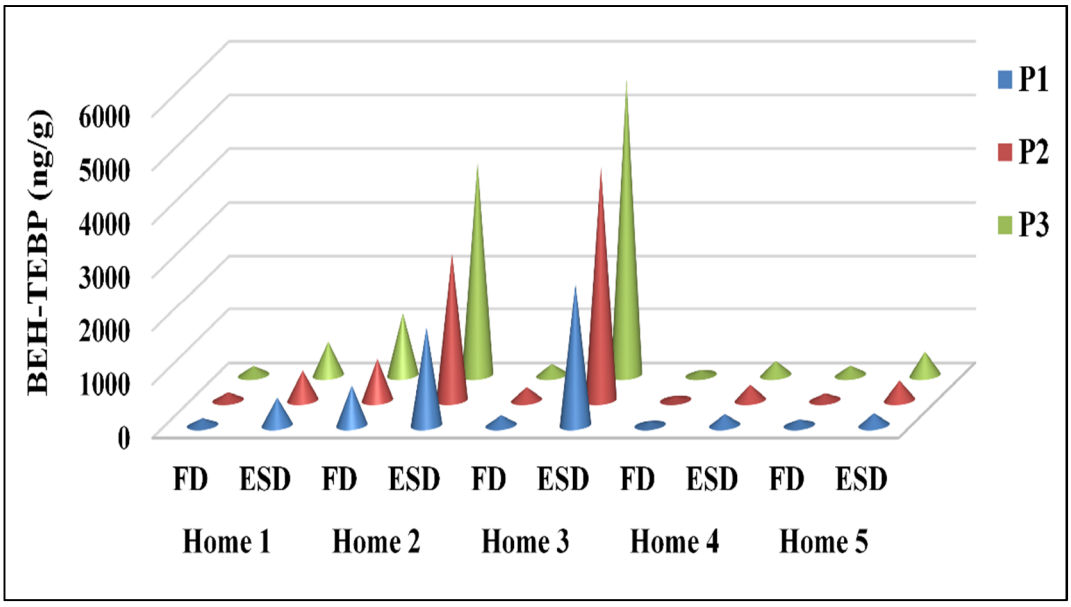
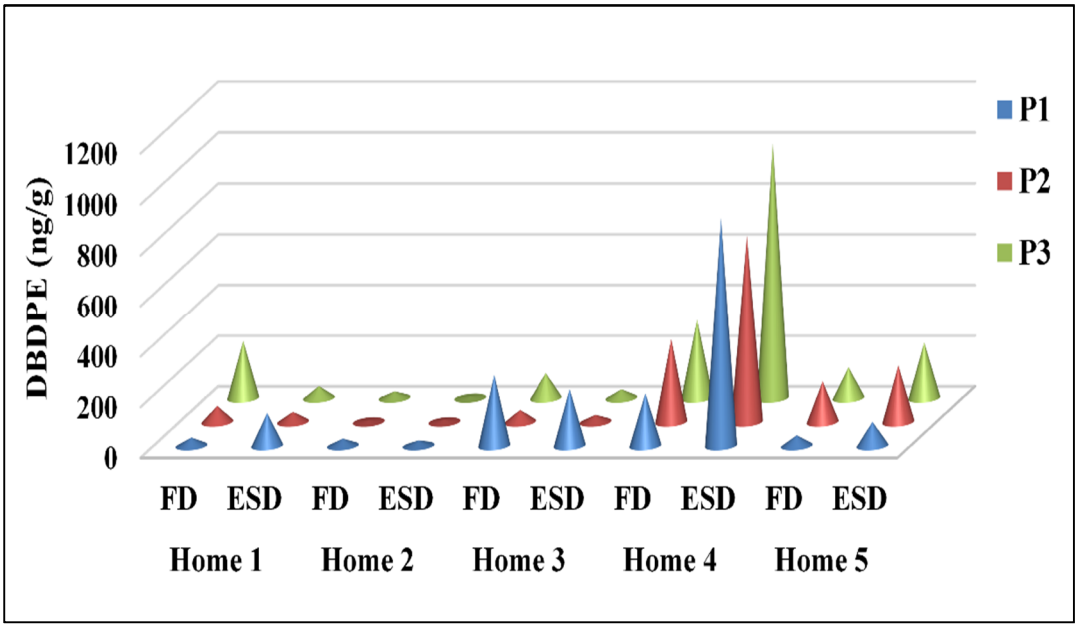



**Figure 5.7: DBDPE concentrations in different particle size fractions of elevated surface dust (ESD) and floor dust (FD) samples from five homes**



### 5.3.3 Distribution patterns of PBDEs and NBFRs with particle size

Following log transformation of BFR concentrations (ng/g dw), one-way repeated measures ANOVA was applied to test the hypothesis that concentrations of BFRs in P3 would exceed significantly those in P2 and P1. This analysis revealed no significant differences ($p > 0.05$) between concentrations in different dust particle size fractions of: BDE-209, BTBPE, DBDPE, and EH-TBB. In contrast, in the finest particle size fraction (P3), concentrations of BDE-47 ($p = 0.03$), BDE-99 ($p = 0.004$), BDE-183 ($p = 0.046$), BEH-TEBP ($p = 0.001$), $\Sigma_5$NBFRs ($p = 0.008$), and $\Sigma_7$tri-hepta-BDEs ($p < 0.001$) exceeded significantly those detected in the coarsest fraction (P1). In addition, concentrations of BDE-99 ($p = 0.009$), BEH-TEBP ($p = 0.017$), $\Sigma_5$NBFRs ($p = 0.007$), and $\Sigma_7$tri-hepta-BDEs ($p < 0.001$) in the finest particles (P3) significantly exceeded those in the medium particle size fraction P2. Concentrations in P3 of BDE-183 ($p = 0.053$) were near-significantly elevated over those in P2. Moreover, concentrations of BDE-99 ($p = 0.008$), BDE-153 ($p = 0.002$) BEH-TEBP ($p = 0.003$), and $\Sigma_7$tri-hepta-BDEs ($p = 0.003$) in the medium particle size fraction (P2) exceeded significantly those in the coarsest size fraction (P1). These findings show that for some BFRs, concentrations increase with decreasing particle size; while for other BFRs, such a relationship does not exist.

Interestingly, concentrations of our target BFRs in bulk dust (25-250 μm) exceeded significantly those in one or more of the 3 particle size sub-fractions for BDE-153, BEH-TEBP, and Σtri-hepta-BDEs only. This suggests that the use in many past studies of a relatively broad particle size range has likely not unduly influenced exposure assessment. Appendix 4 lists *p* values obtained from the ANOVA comparison of concentrations of individual PBDEs and NBFRs in different particle size fractions.

It has been reported that organic pollutant measurements in settled dust could provide a prediction of their concentrations in suspended particles and the gas phase (Morawska and Salthammer 2003; Weschler et al., 2008; Allen et al., 2008). As semi-volatile organic compounds (SVOCs) and additive flame retardants, our target BFRs can be released from the products via volatilisation into surrounding air, depending on their vapour pressure ($V_P$). Such volatilised BFRs may then undergo deposition to both suspended and settled indoor dust, with the relative partitioning between these two phases governed by the octanol-air partition coefficient ($K_{OA}$) of the BFRs (Li et al., 2006; Weschler and Nazaroff, 2010). This

volatilisation with subsequent deposition process will be more important for BFRs with higher vapour pressures/lower $K_{OA}$ values. By comparison, the presence of less volatile BFRs may be governed more by other processes such as direct contact between BFR source and dust and abrasion of BFR source materials (Rauert and Harrad, 2015; Suzuki et al., 2009; Webster et al., 2009). These factors, combined with the fact that atmospheric deposition of BFRs to dust particles will be greater for finer particle sizes due to their greater surface area to volume ratio (Lewis et. al., 1999; Wei et al., 2009; Mercier et al., 2011); means that significantly higher concentrations on finer dust particles would be anticipated for more volatile BFRs, with this likely less influential for their less volatile counterparts. With the exception of BEH-TEBP – for which the available data on its vapour pressure suggests it would behave in the same way as BDE-209, BTBPE, and DBDPE (Tables 1.6 and 1.7, Chapter 1). This is consistent with our data, which show higher concentrations of BDEs 47, 99, and BEH-TEBP in finer dust particles, but no particle size preference for BDE-209, BTBPE, DBDPE, and EH-TBB.

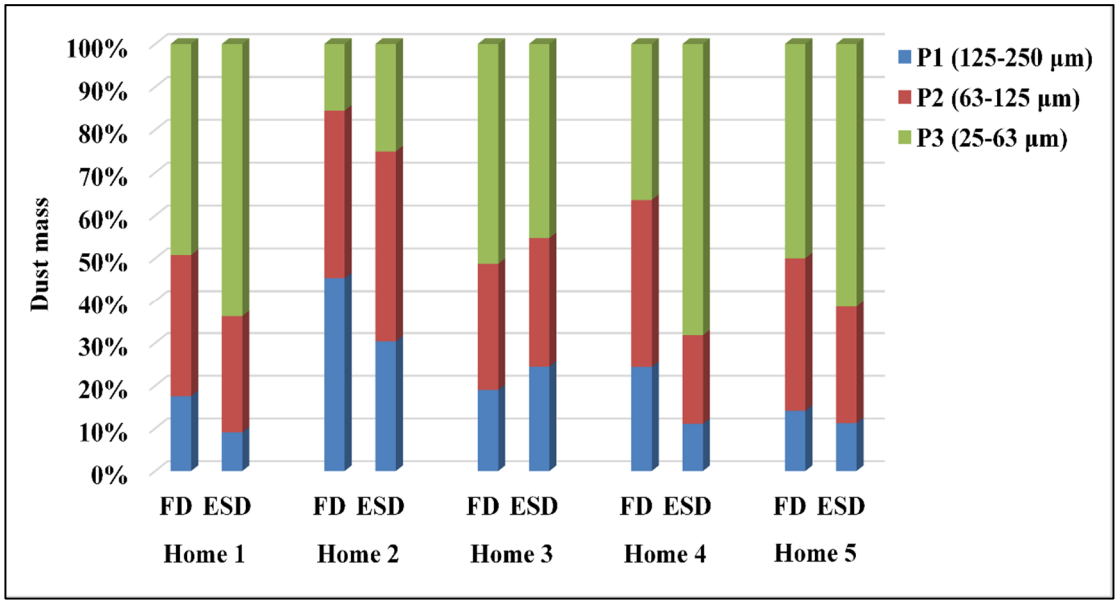
Selection of an indoor dust particle size fraction for analysis depends on the aim of the study. In addition, comparison of results between studies requires selection of a common size fraction for analysis alongside similar sample preparation methods (Mercier et al., 2011). It is thus difficult to compare our data with previous studies. However, despite very limited studies that have investigated BFR concentrations as a function of particle size, some common points of comparison emerge. Wei et al., (2009) was the first study to investigate distribution patterns of PBDEs in different particle size fractions (250- 420, 150- 250, 75- 150 and < 75 $\mu$m) of dust from one car and two homes in Chicago, USA. The study reported that PBDE concentrations in the car dust increased with decreasing particle size, while in the house dust, the concentrations were comparable between fractions. The study suggested that indoor house dust contains fibre-like material in fraction > 150 μm, which may be weathered into large particles. Another study (Kefeni et al., 2014) that examined the effect of dust particle size (106–150, 45- 106 and < 45 μm) on PBDE concentrations, found the highest concentrations in the medium fraction, which the authors stated may be due to the lower sample size of their study. In China, in office dust, Cao et al., (2013) reported some variation in concentrations of PBDEs with particle size. Concentrations of tri-hexa PBDEs were highest in the 74-100 μm and 100-200 μm particle size fractions, those of hepta-PBDEs were greatest in 200-300 μm and 300-400 μm fractions. Octa- and deca-PBDE concentrations peaked in particles < 50 μm, while 2-bis (2,4,6-tribromophenoxy) ethane (BTBPE) was highest in the 50-74 μm and 75-

100 µm size ranges, which is inconsistent with our finding, this might be due to variations between different microenvironments. In a subsequent study by the same authors, Cao et al., (2014a) reported that in several non-domestic microenvironments, BDE-209 showed higher levels in coarser particles from kindergartens (500-900 µm) and dormitories (900-2000 µm). Moreover, BFR concentrations did not increase constantly with decreasing particle size. Instead, the variation of concentrations with particle size was multi-modal, with the highest levels associated with particle sizes around 900, 100, and 10 µm. The study suggested that abrasion processes might be an important factor influencing distribution patterns of FRs (Cao et al., 2014a). A later study revealed no significant variation in concentrations of HBCDs between different particle size fractions (Cao et al., (2015). In addition, Chao et al., (2014) found no significant difference in concentrations of $\Sigma_{28}$PBDE in different particle sizes of house dust and electronic dust.

### 5.3.4 Influence of mass ratio of dust on BFR particle size distribution

The average mass percentage of dust fractions P1, P2 and P3 in the bulk dust were about 20.6%, 32.7% and 46.6%, respectively. Figure 5.8 illustrates the mass percentage contribution of dust fractions P1, P2 and P3 to BD.

**Figure 5.8: Mass percentage of P1, P2 and P3 in bulk dust (< 250 µm) from elevated surfaces (ESD) and floors (FD) in Homes 1-5**



It was reported previously that indoor dust particle size distribution may vary between countries and indoor environments (Lioy et al., 2002; Morawska and Salthammer 2003). While in this study, on average ~79% of the bulk dust mass was associated with particles < 125 μm, in South Africa, Kefeni et al., (2014) found (among four dust fractions < 45, 45–106, 106–150 and 150–250 μm) that 93% of the dust fraction was associated with particles < 150 μm. In a similar study in Taiwan, Chao et al., (2014) found (among three fractions, < 74, 47-149, and < 149 μm) that < 74 μm particles accounted for 50-76% of overall dust by mass. From two homes and one car in the USA, Wei et al., (2009) reported (among four dust fractions, < 75, 75–150, 150–250 and 250–420 μm) that > 50% of particles in their house dust samples were < 75 μm, while in their car dust sample, each size fraction contributed equally to the overall mass. Our findings are comparable to the USA house dust samples of Wei et al (2009) as ~47% of the particle size fraction were found in particle size fraction < 63 μm. Table 5.3 shows the BFR mass distribution values for selected BFRs in our 3 particle size fractions. These values are the product of the dust size fraction and the corresponding BFR concentration (ng/g) in that fraction and are a measure of the proportion of the BFR mass in a bulk dust sample that is associated with a given particle size fraction. Table 5.3 shows that the finest particle size fraction (P3) represents the greatest values for all target compounds.

**Table 5.3: BFR mass distributions in fractions P1, P2 and P3.**

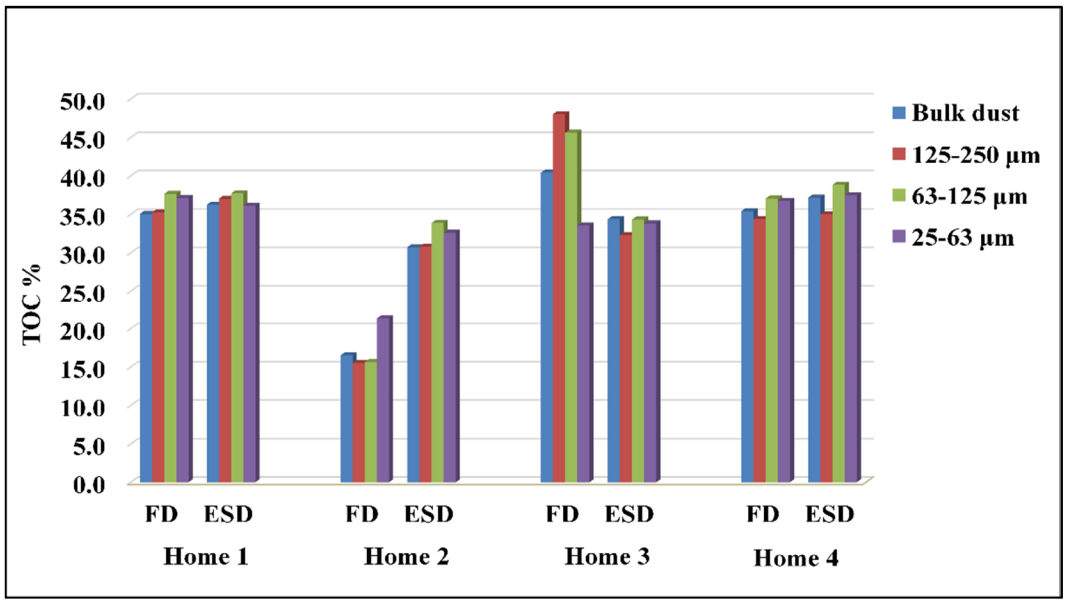
| | **BFR Mass Distribution Value (ng/g)** | | |
|---|---|---|---|
| **Target compound** | **P1** | **P2** | **P3** |
| BDE-47 | 2.2 | 4.4 | 6.8 |
| BDE-99 | 4.2 | 9.9 | 19.1 |
| BDE-153 | 1.0 | 2.6 | 3.8 |
| BDE-183 | 2.0 | 4.2 | 8.0 |
| $\Sigma_7$tri-hepta-BDEs | 9.9 | 22.5 | 40.5 |
| BDE-209 | 662 | 912 | 1247 |
| EH-TBBB | 2.0 | 4.0 | 5.5 |
| BTBPE | 3.2 | 6.3 | 8.7 |
| BEH-TEBP | 138 | 318 | 590 |
| DBDPE | 40 | 54 | 98 |
| $\Sigma_5$NBFRs | 184 | 383 | 702 |

### 5.3.5 Determination of organic carbon content in dust samples

The total organic carbon (TOC) content of our dust samples was determined by using a Total Organic Carbon analyzer TOC-$V_{CSH/CSN}$ fitted with a Solid Sample Module SSM-5000, both from SHIMADZU, Japan. The instrument provided measurements of Total Carbon (TC) and Inorganic Carbon (IC), with TOC was deduced by subtracting the IC value from TC (Method description in Chapter 2 section 2.8). Due to the low dust mass available from House 5, TOC was not determined in dust samples from this house.

Average percentages of TOC in each dust fraction were 33.2%, 33.5%, 35.1% and 33.6% for BD, P1, P2 and P3 respectively. The highest percentage (48.0%) was found in floor dust of Home 3 and the lowest (15.5%) in floor dust of Home 2, both in the largest particle size fraction. Figure 5.9 illustrates TOC contents of different particle size fractions in both FD and ESD.

**Figure 5.9: TOC% contents of different particle size fractions in both floor dust (FD) and elevated surface dust (ESD)**




The composition of indoor dust is complex, which can be affected by many factors such as, paints, carpet, furniture, number and age of occupants. In general, the organic content of indoor dust ranges between < 5 and > 95% (Morawska and Salthammer 2003), which is much higher than in outdoor dust (Cao et al., 2014a). Thus, lower organic contents in floor dust in

Home 2 might be due to the high ratio of sand tracked in by children. Based on our findings, the TOC levels in the UK were slightly lower than the 50% found in China (Cao et al., 2014a; 2015) and the 52% in USA house dust (Wei et al., 2009). On the other hand, our values were much higher than in Iraqi dust samples (Chapter 7) and comparable to those in South Africa (Kefeni et al., 2014).

We hypothesised that variations in TOC between different particle size fractions and between FD and ESD could at least in part account for some of the corresponding variations in BFR concentrations we observed. That this is feasible, is underlined by the fact that significant positive linear correlations were observed between BFR concentrations in all samples and their corresponding total organic carbon (TOC) content, with R values ranging between 0.883 and 0.979 ($p < 0.001$). We therefore examined our data to check whether normalising BFR concentrations to the organic carbon content of the dust fraction analysed, exerted any influence on our observations related to variations in BFR concentration with particle size. We found that doing so, made no difference to our findings based on concentrations normalised to dry weight of dust alone. Only in one case, TOC in P1 exceeded significantly those in BD with a $p$ value of 0.027 (Appendix 5). We deduce therefore, that differences in organic carbon content of dust cannot explain either the variation in BFR concentrations with particle size fraction. Figures 5.10 and 5.11 illustrate relationships between $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and DBDPE concentrations and the corresponding TOC values in P1, P2 and P3 in dust samples from the four homes for which this was possible.

**Figure 5.10: $\Sigma_7$tri-hepta-BDEs and BDE-209 concentrations and the corresponding total organic carbon (TOC) contents in P1 (125-250 µm), P2 (63-125 µm) and P3 (25-63 µm) and in floor dust (FD) and elevated surface dust (ESD) from four homes (H1, H2, H3 and H4)**

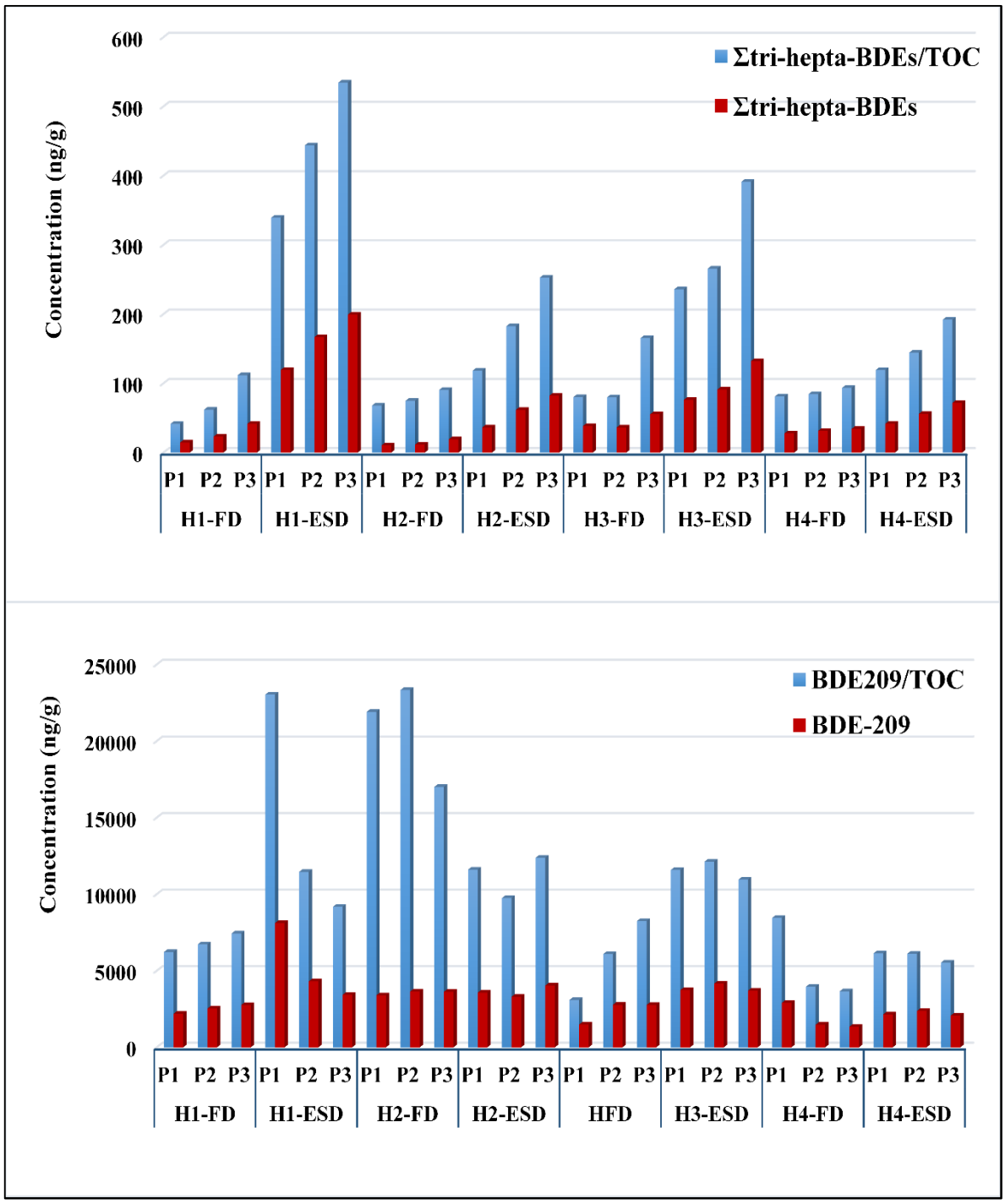
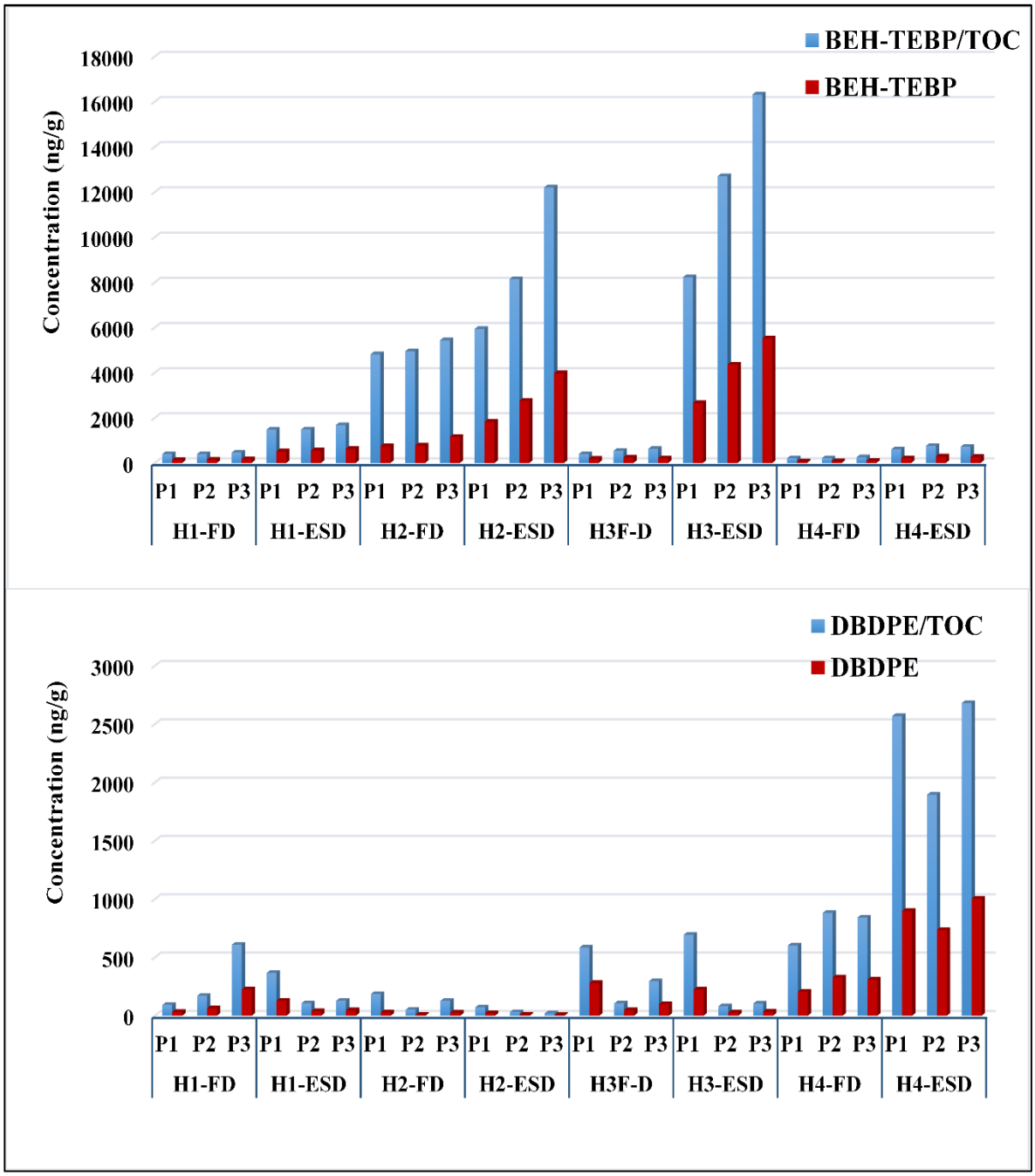


**Figure 5.11: BEH-TEBP and DBDPE concentrations and the corresponding total organic carbon (TOC) contents in P1 (125-250 µm), P2 (63-125 µm) and P3 (25-63 µm) and in floor dust (FD) and elevated surface dust (ESD) from four homes (H1, H2, H3 and H4)**



## 5.4 Dust particle size impact on human exposure assessments to BFRs

For human exposure assessments, since 2000, it has been recommended that dust particle size fraction < 250 µm are most likely to stick to hands and be ingested and/or absorbed dermally (Que Hee et al., 1985; USEPA, 2000; 2003). However, different particle size fractions have been applied for exposure assessment purposes, ranged between < 63 µm and 2000 µm (Chapter 1, section 1.10.2.3). Based on recent information, TRW (Technical Review Workgroup for Metals and Asbestos) recommended moving from < 250 µm to < 150 µm as the adhered dust is dominated by < 150 µm fraction. (USEPA, 2016).

To evaluate to what extent human exposure to our target contaminants via dust ingestion is influence by the choice of particle size for analysis, we used our data on concentrations of BFRs from bulk dust (< 250 µm), P1 (250-125 µm), P2 (63-125 µm) and P3 (25-63 µm), assuming 100% absorption and applying the same three scenarios (low-end exposure, "typical" and high-end exposure) described in Chapter 1, section 1.9. To fully reflect indoor contamination of BFRs, the overall concentration of each contaminant was taken to be the average of the elevated surface and floor dust sample concentrations from the same rooms. Table 5.4 lists our exposure estimates (ng/kg body weight/day) for adults and toddlers to $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP, DBDPE and $\Sigma_5$NBFRs via ingestion of bulk dust (BD) and dust falling into different particle size fractions (P1 = 125-250 µm, P2 = 63-125 µm and P3 = 25-63 µm).

**Table 5.4: Estimated exposure (ng/kg body weight/day) of adults and toddlers to PBDEs and NBFRs via ingestion of bulk dust (BD) and dust falling into different particle size fractions (P1 = 125-250 µm, P2 = 63-125 µm and P3 = 25-63 µm)**

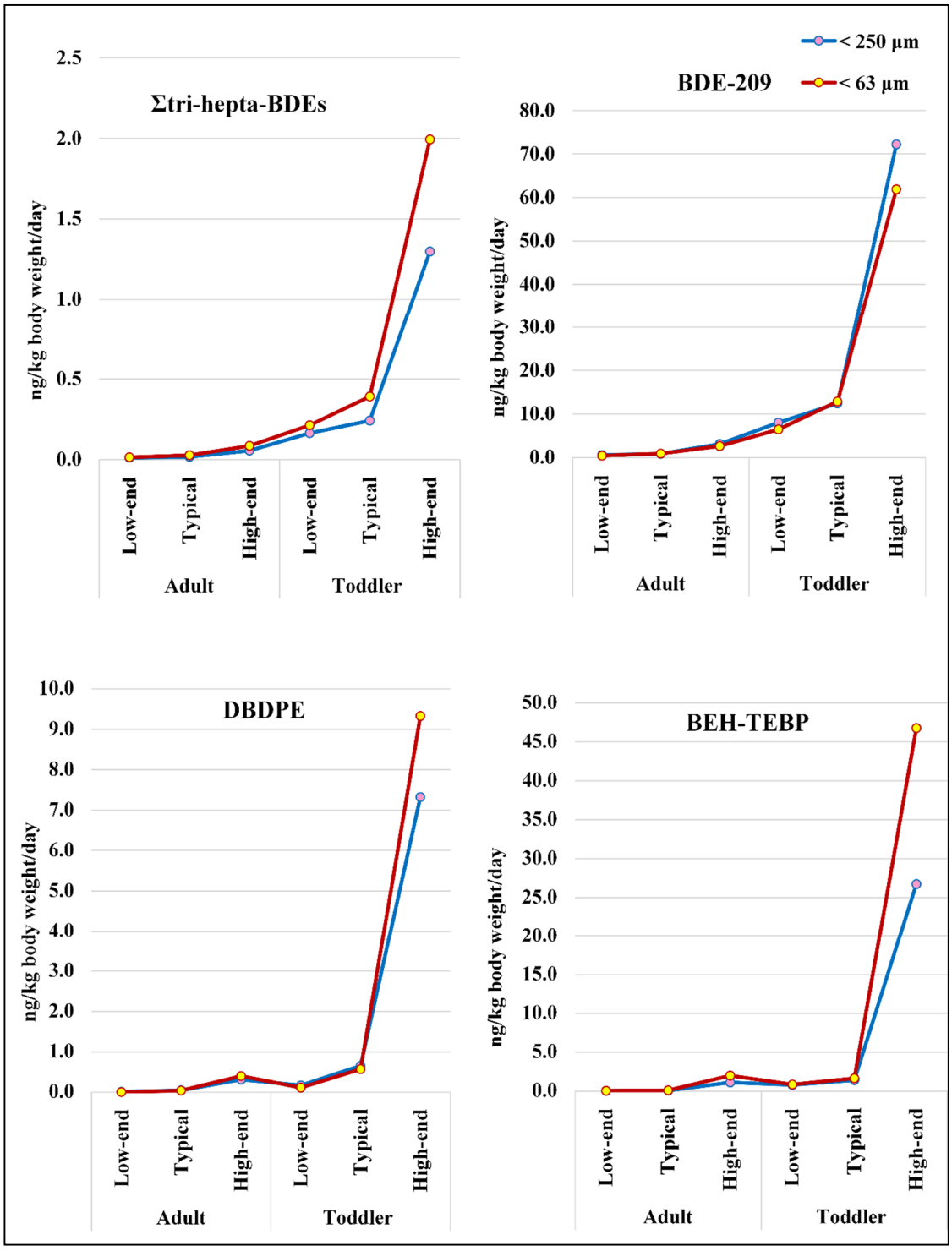
| Target compound | Dust fraction | Adult | | | Toddler | | |
|---|---|---|---|---|---|---|---|
| | | Low-end | Typical | High-end | Low-end | Typical | High-end |
| $\Sigma_7$tri-hepta-BDEs | BD | 0.011 | 0.017 | 0.056 | 0.16 | 0.24 | 1.30 |
| | P1 | 0.007 | 0.016 | 0.047 | 0.11 | 0.24 | 1.09 |
| | P2 | 0.011 | 0.018 | 0.073 | 0.16 | 0.27 | 1.70 |
| | P3 | 0.015 | 0.027 | 0.085 | 0.21 | 0.39 | 1.99 |
| BDE-209 | BD | 0.551 | 0.854 | 3.096 | 8.04 | 12.46 | 72.23 |
| | P1 | 0.660 | 0.747 | 3.443 | 9.63 | 10.89 | 80.34 |
| | P2 | 0.486 | 0.977 | 2.480 | 7.09 | 14.25 | 57.86 |
| | P3 | 0.443 | 0.884 | 2.651 | 6.45 | 12.89 | 61.85 |
| BEH-TEBP | BD | 0.056 | 0.097 | 1.146 | 0.81 | 1.42 | 26.75 |
| | P1 | 0.042 | 0.094 | 0.998 | 0.62 | 1.37 | 23.28 |
| | P2 | 0.057 | 0.101 | 1.568 | 0.83 | 1.47 | 36.59 |
| | P3 | 0.059 | 0.114 | 2.004 | 0.86 | 1.66 | 46.76 |
| DBDPE | BD | 0.012 | 0.045 | 0.314 | 0.17 | 0.65 | 7.33 |
| | P1 | 0.010 | 0.023 | 0.352 | 0.14 | 0.34 | 8.22 |
| | P2 | 0.004 | 0.015 | 0.331 | 0.06 | 0.22 | 7.73 |
| | P3 | 0.008 | 0.039 | 0.400 | 0.11 | 0.57 | 9.33 |
| $\Sigma_5$NBFRs | BD | 0.123 | 0.203 | 1.283 | 1.79 | 2.96 | 29.93 |
| | P1 | 0.083 | 0.204 | 1.183 | 1.21 | 2.97 | 27.60 |
| | P2 | 0.123 | 0.211 | 1.642 | 1.79 | 3.07 | 38.32 |
| | P3 | 0.148 | 0.248 | 2.074 | 2.16 | 3.62 | 48.40 |

$\Sigma_7$tri-hepta-BDEs BDE-28, -47, -99, -100, -153, -154, and -183
$\Sigma_5$NBFRs PBEB, EH-TBB, BTBPE, BEH-TEBP and DBDPE

For each of $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and DBDPE, we calculated the ratio of the average exposure estimate based on ingestion of dust from fraction P3 to that obtained assuming ingestion of BD. The obtained ratios were 1.54, 0.86, 1.75 and 1.27 for $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and DBDPE respectively. This indicates that with the exception of BDE-209, the choice of a finer particle size fraction for assessment of exposure to BFRs,

will provide a higher exposure estimate. Figure 5.12 compares exposure assessments for $\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEBP and DBDPE based on ingestion of both P3 and BD.

**Figure 5.12: BFR exposure assessment comparison between dust particle size fractions < 63 µm and < 250 µm for both adults and toddlers**



## 5.5 Conclusion

This chapter examines the distribution of selected PBDEs and NBFRs in different particle size fractions below 250 μm in both elevated surface and floor dust. While concentrations of tri-hepta-BDEs and BEH-TEBP are significantly higher in dust particles 25-63 μm diameter than in particles 125-250 μm and 63-125 μm; concentrations of BDE-209, BTBPE, EH-TBB, and DBDPE are not significantly different between different dust particle size fractions. The organic carbon of dust cannot explain the higher concentrations of some BFRs in elevated surface compared to floor dust, nor the higher concentrations in finer dust particles. It is apparent that while concentrations of many BFRs vary according to the dust particle size fraction, the exact nature of this variation remains unclear and the reasons for such variation have yet to be conclusively elucidated. It instead seems more plausible that BFR concentrations will be greater in dust particles with a greater surface area to mass ratio, a hypothesis consistent with the higher proportion of finer particles found in elevated surface compared to floor dust in Basrah, Iraq (Chapter 7).

For human exposure assessment to BFRs in settled dust, the selection of the particle size fraction for analysis is important, with our study indicating that analysing finer particles (25-63 μm) yields higher exposure estimates than if a larger, broader size range (25-250 μm) is analysed.

# CHAPTER 6

# THE INFLUENCE OF DUST SAMPLING APPROACH AND DUST SURFACE LOADING ON CONCENTRATIONS OF LEGACY AND "NOVEL" BROMINATED FLAME RETARDANTS IN INDOOR DUST

## 6.1 Summary

This chapter investigates the impact of the sampling method on the concentrations of PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209) and NBFRs (PBEB, EH-TBB, BEH-TEBP, BTBPE and DBDPE) in indoor dust. From 12 homes in Birmingham, UK, dust samples were collected by the researcher (researcher collected dust-RCD) from the living room (RCDL) and bedroom (RCDB), with an additional sample taken that comprised the contents of a vacuum cleaner bag donated by the householder (householder vacuum dust- HHVD). In addition, we investigate the relationship between BFR concentrations (ng/g) and BFR dust loading (g/m$^2$), using the temporal variation data reported in Chapter 4. Concentrations of PBDEs and NBFRs were determined in these samples to test the following hypotheses: (a) BFR concentrations in RCD will be different from those in HHVD (b) BFR concentrations in RCD and HHVD will be significantly correlated, and (c) as a consequence of a "BFR dilution effect", a logarithmic plot of dust loadings against BFR concentrations will be linear with a negative slope.

The findings showed that BDE-209 was the predominant compound, with average concentrations of 2642, 2336 and 2634 ng/g in RCDL, RCDB and HHVD respectively. The next most abundant BFR was BEH-TEBP, followed by DBDPE, with average concentrations of 306, 339 and 233 ng/g for BEH-TEBP and 155, 91 and 152 ng/g for DBDPE in RCDL, RCDB and HHVD respectively. Average concentrations of other individual contaminants ranged between 0.4 ng/g for PBEB in RCDB and HHVD, and 23 ng/g for BDE-99 in RCDL. Average concentrations of $\Sigma_6$tri-hexa-BDEs (ΣBDE-28, BDE-100, BDE-47, BDE-99, BDE-153 and BDE-154) were 47, 41, and 24 ng/g in RCDL, RCDB and HHVD respectively.

One way repeated measures ANOVA tests were applied to compare means of BFR concentrations in RCDL, RCDB and HHVD. The ANOVA test revealed that, with the exception of $\Sigma_6$tri-hexa-BDEs, BDE-153, BDE-99 ($p$ = 0.012 - 0.038) and BEH-TEBP ($p$ =

0.077), no significant differences were found between BFR concentrations in RCD and HHVD. With the exception of BDE183 ($p$ = 0.001), no significant differences in BFR concentrations were observed between RCDL and RCDB. These findings indicate that while HHVD could be a viable alternative to RCD for higher brominated BFRs, it significantly underestimated concentrations of lower brominated FRs in our study.

A Pearson correlation was used to test the relationship between BFR concentrations in dust collected via the two sampling methods. Statistically significant correlations were observed between HHVD and RCD for $\Sigma_6$tri-hexa-BDEs ($R$ = 0.583, $p$ = 0.047 and $R$ = 0.588, $p$ = 0.044), BEH-TEBP ($R$ = 0.793, $p$ = 0.002 and $R$ = 0.883, $p$ = < 0.001) and DBDPE ($R$= 0.643, $p$ = 0.024 and $R$ = 0.634, $p$ = 0.027) in RCDL and RCDB respectively. Additionally, concentrations of BDE-99 in HHVD were significantly correlated ($R$ = 0.611, $p$ = 0.035) with those of RCDL. Furthermore, concentrations of BDE-209 in RCDL and of EH-TBB in RCDB were moderately correlated with HHVD ($R$ = 0.532, $p$ = 0.075 for BDE-209 and $R$ = 0.557, $p$ = 0.060 for EH-TBB).

Despite a lack of evidence (body burden measurements) about which method is more biologically relevant, we used our concentration data to derive separate estimates of exposure via dust ingestion based on different sampling methods. This revealed that the high-end exposure ratios (RCDL/ HHVD) were 3.5, 2.7 and 1.3 for BDE-99, $\Sigma_6$tri-hexa-BDEs and BEH-TEBP respectively, which indicates that the choice of householder vacuum for assessment of exposure to BFRs, will provide a lower exposure estimate, particularly for Penta-BDEs and to some extent for BEH-TEBP.

To test the relationship between BFR dust concentration (ng/g) and dust loading (g/m$^2$), we used our data given in Chapter 4 addressing temporal variability in BFR concentrations in dust from Home 1, Home 2, and Home 3. The Pearson correlation showed a significant negative correlation between the logarithms of BFR concentrations and dust loadings for Home 2 and Home 3 for BDE-99 ($R$ = 0.675, $p$ = 0.046) and $\Sigma_7$tri-hepta-BDEs ($R$ = 0.760, $p$ = 0.018) in H2R2F2 and for BEH-TEBP ($R$ = 0.749, $p$ = 0.020) in H3R2F2. This implies that BDE-99, $\Sigma_7$tri-hepta-BDEs and BEH-TEBP were diluted by high dust loadings.

## 6.2 Sampling and Sample preparation

In this study, we compared two widely employed dust sampling methods; researcher-collected (Brommer et al., 2012; Harrad et al., 2016) and household vacuum cleaner bag method (Sjödin et al., 2008a; Shoeib et al., 2012; Fromme et al., 2014). From Birmingham, UK, dust samples (n = 36) were collected from 12 homes in September and November 2014 for 8 homes, and during April 2015 for 4 homes. In each home, two dust samples were collected by the researcher (researcher-collected dust- RCD) with the householder additionally providing the contents of their vacuum cleaner (household vacuum dust- HHVD). RCD samples were obtained from the living room (RCDL) and bedroom (RCDB) of each house, according to a clearly defined standard protocol (Harrad et al., 2008a), that was described in Chapter 2, section 2.3. Briefly, by using a handheld vacuum cleaner (DIRT DEVIL-DDMHH1-1100W), 1 $m^2$ of carpeted floor area was vacuumed for 2 min, using 25 μm pore size nylon sample socks mounted in the furniture attachment tube of the vacuum cleaner. All RCD samples were taken from carpeted floor areas. After sampling, socks were closed with a twist tie, sealed in plastic bags. Before sampling, the furniture attachment and the vacuum tubing were cleaned thoroughly using isopropanol-impregnated disposable wipes and dried between collections. HHVD samples were collected at the same time. The dust bag from the householder's own vacuum cleaner was wrapped in aluminium foil and sealed in plastic bags. All dust samples were stored at −20 ˚C until analysis. Prior to analysis, dust samples were passed through a pre-cleaned, *n*-hexane rinsed 250 μm mesh testing sieve covered with the lid and shaken for 3-5 min. Information on the potential influences on BFR contamination were recorded on the questionnaire shown in Appendix 1.

## 6.3 Results and discussion

### 6.3.1 Detection frequencies and the relationship between BFRs

In all dust samples (n = 36), the detection frequency of PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209) and NBFRs (PBEB, EH-TBB, BTBPE, BEH-TEBP, and DBDPE) ranged from 50% to 100%. The detection frequencies of BDE-209, BEH-TEBP and DBDPE were 100% in both researcher-collected dust (RCD) and household vacuum dust (HHVD). BDE-28, BDE-100, BDE-154 and PBEB were in the lowest detection frequencies (< 67%). Thus, they were not accounted for individual statistical comparison, however, they were included in $\Sigma_6$tri-hexa-BDEs (BDE-28, BDE-47, BDE-99,

BDE-100, BDE-153, and BDE-154) and $\Sigma_5$NBFRs (PBEB, EH-TBB, BTBPE, BEH-TEBP, and DBDPE). Table 6.1 lists detection frequencies of PBDEs and NBFRs in this study.

**Table 6.1: Detection frequencies (%) of PBDEs and NBFRs in researcher-collected dust samples from the living room (RCDL) and bedroom (RCDB) and household vacuum dust (HHVD)**

| Target compound | RCDL | RCDB | HHVD |
|---|---|---|---|
| BDE-28 | 67 | 83 | 67 |
| BDE-47 | 92 | 92 | 83 |
| BDE-99 | 100 | 92 | 100 |
| BDE-100 | 83 | 83 | 58 |
| BDE-153 | 92 | 100 | 75 |
| BDE-154 | 75 | 75 | 58 |
| BDE-183 | 92 | 75 | 75 |
| BDE-209 | 100 | 100 | 100 |
| PBEB | 75 | 50 | 58 |
| EH-TBB | 83 | 75 | 75 |
| BTBPE | 83 | 92 | 75 |
| BEH-TEBP | 100 | 100 | 100 |
| DBDPE | 100 | 100 | 100 |

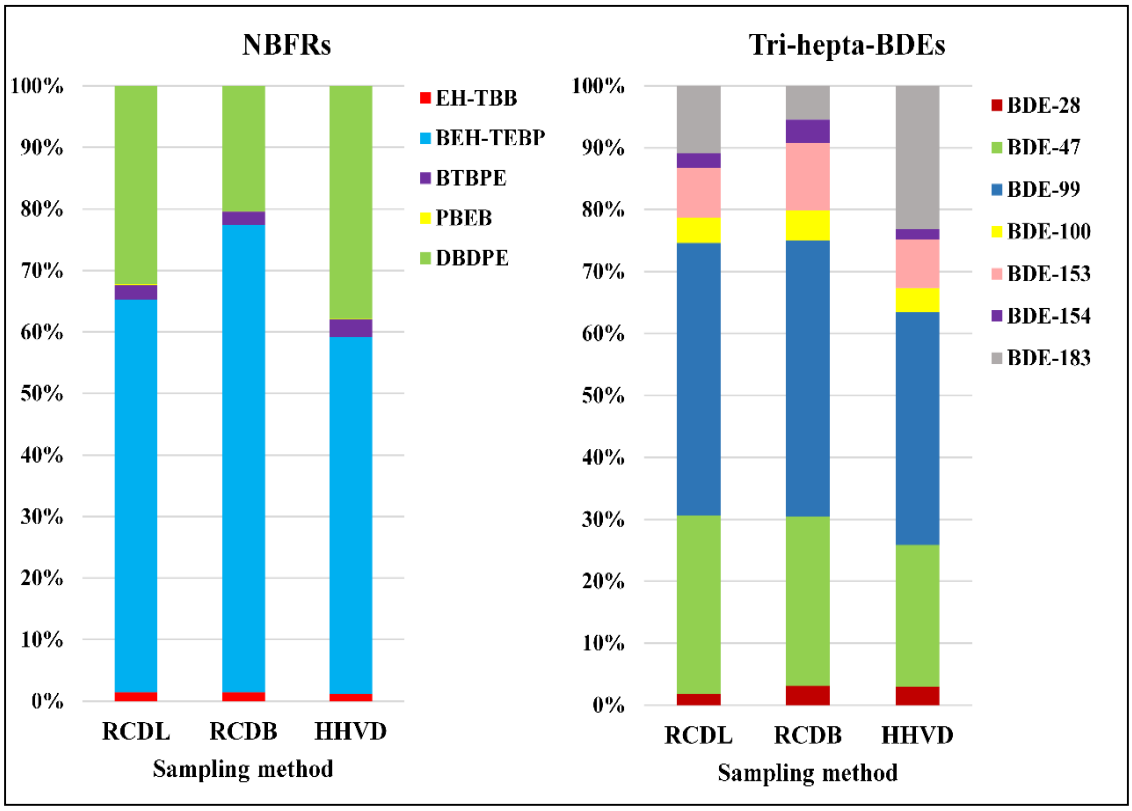
The three main commercial PBDE formulations (Penta-BDE, Octa-BDE and Deca-BDE) are represented in this study by $\Sigma_6$tri-hexa-BDEs as an indicator of Penta-BDE, BDE-183 as an indicator of Octa-BDE and BDE-209 as an indicator of Deca-BDE. Among our target BFRs, BDE-209 was the predominant compound, with average percentage contributions to ΣBFRs (sum of $\Sigma_6$tri-hexa-BDEs, BDE-209, BDE-183 and $\Sigma_5$NBFRs) of 83.2%, 82.7% and 85.9% in RCDL, RCDB and HHVD respectively. $\Sigma_5$NBFRs were the next most abundant parameter, with average contributions of 15.1%, 15.8% and 13% in RCDL, RCDB and HHVD respectively. $\Sigma_6$tri-hexa-BDEs and BDE-183 displayed the lowest average percentage contributions of our target BFRs, which ranged between 0.1% and 1.5%. Table 6.2 shows the average percentage contributions of BDE-209, $\Sigma_6$tri-hexa-BDEs BDE-183 and $\Sigma_5$NBFRs to ΣBFRs.

**Table 6.2: Average percentage contributions (%) of BDE-209, $\Sigma_5$NBFRs, BDE-183 and $\Sigma_6$tri-hexa-BDEs to ΣBFRs in RCDL and RCDB (researcher-collected dust samples form the living room and bedroom) and HHVD (household vacuum dust)**

| Target compound | RCDL | RCDB | HHVD |
|---|---|---|---|
| BDE-209 | 83.2 | 82.7 | 85.9 |
| $\Sigma_6$tri-hexa-BDEs | 1.5 | 1.5 | 0.8 |
| BDE-183 | 0.2 | 0.1 | 0.2 |
| $\Sigma_5$NBFRs | 15.1 | 15.8 | 13.1 |

Of our target NBFRs, BEH-TEBP was the predominant compound, with corresponding mean percentage contributions to $\Sigma_5$NBFRs of 64%, 76% and 58%, followed by DBDPE with percentage contributions of 32%, 20% and 38% for RCDL, RCDB and HHVD respectively. Mean percentage contributions of the rest of our target NBFRs ranged between 0.09% for PBEB in RCDB and 2.8% for BTBPE in HHVD. With the exception of BDE-209, concentrations of BDE-99 and BDE-47 made the highest average contributions to the target PBDEs, followed by BDE-183. The average percentage contributions of BDE-99, BDE-47 and BDE-183 to $\Sigma_7$tri-hepta-BDEs ($\Sigma_6$tri-hexa-BDEs pulse BDE-183) were 44%, 45% and 38% for BDE-99, 29%, 27% and 23% for BDE-47, and 11%, 5.4% and 23% for BDE-183 in RCDL, RCDB and HHVD respectively. The rest of our target PBDEs ranged between 1.7% for BDE-154 in HHVD and 11% for BDE-153 in RCDB. Figure 6.1 depicts the average percentage contributions and congener/compound profiles of tri-hepta-BDEs and NBFRs in RCDL, RCDB and HHVD.

**Figure 6.1: Average percentage contributions and congener/compound profiles of tri-hepta-BDEs and NBFRs in RCDL, RCDB (researcher-collected dust from the living room and bedroom) and HHVD (household vacuum dust)**




### 6.3.2: Concentrations of PBDEs and NBFRs in indoor dust obtained via two different sampling methods

In all dust samples, the highest concentrations of total target ΣPBDEs and $\Sigma_5$NBFRs were found in researcher-collected dust samples from living rooms (RCDL), with values of 4321 and 1450 ng/g for ΣPBDEs and $\Sigma_5$NBFRs respectively. As mentioned above, among all our target pollutants, BDE-209 was the predominant compound, with average concentrations of 2642, 2336 and 2634 ng/g in RCDL, RCDB and HHVD respectively. The average concentrations of BEH-TEBP were 309, 339 and 233 ng/g in RCDL, RCDB and HHVD respectively. Average concentrations of DBDPE were comparable in both RCDL and HHVD samples, with values of 155 and 152 respectively, while in RCDB it was 91 ng/g. $\Sigma_6$tri-hexa-BDEs average concentrations in RCDL, RCDB and HHVD was 47.3 and 41.3 and 24.4 ng/g in RCDL, RCDB and HHVD respectively. Among tri-hepta-BDEs ($\Sigma_6$tri-hexa-BDEs + BDE183), BDE-99, BDE-47 and BDE-183 average concentrations were 23.3, 19.5 and 11.8 ng/g for BDE-99, 15.3, 12.0 and 7.4 ng/g for BDE-47 and 5.7, 2.4 and 7.2 ng/g for BDE-183

in RCDL, RCDB and HHVD respectively. Average concentrations of other PBDEs (BDE-28, BDE-100 and BDE-154) ranged between 0.54 ng/g for BDE-154 in household vacuum dust and 2.14 ng/g for BDE-100 in researcher-collected dust from living rooms. For the rest of our target NBFRs, BTBPE was found in comparable average concentrations in RCDL and HHVD, with values of 11.0 and 11.2 respectively, while in RCDB, it was 9.5 ng/g. Average concentrations of EH-TBB in RCDL and RCDB were comparable (6.9 and 6.4 ng/g) and higher than in HHVD samples (4.9 ng/g). PBEB concentrations were very low, with average concentrations < 0.6 ng/g in the two sampling methods. Tables 6.3 and 6.4 provide statistical summaries of concentrations of PBDEs and NBFRs in RCDL, RCDB, and HHVD samples. Figures 6.2, 6.3 and 6.4 illustrate the average and standard deviation (y-error bar) concentrations of BFRs ($\Sigma_6$tri-hexa-BDEs, BDE-183, BDE-209 and $\Sigma_5$NBFRs), PBDEs (BDE-99, BDE-47, BDE-153 and BDE-183) and NBFRs (EH-TBB, BTBPE, BEH-TEBP and DBDPE) in RCDL, RCDB, and HHVD respectively.

Comparing with previous studies (Harrad et al., 2008a; 2008b) in Birmingham, UK, the median concentration of PBDEs in this study was lower by a factor of 2.7 for $\Sigma_8$PBDEs, while DBDPE increased by a factor of 3.6.

**Table 6.3: Summary statistics for PBDE concentrations (ng/g) in RCDL, RCDB (researcher collected dust from the living room bedroom) and dust HHVD (household vacuum dust)**

| Target compound | Sampling method | Average | Median | Minimum | Maximum | Standard deviation |
|---|---|---|---|---|---|---|
| BDE-47 | RCDL | 15.3 | 13.0 | < 0.1 | 44.8 | 11.9 |
| | RCDB | 12.0 | 11.1 | < 0.1 | 31.9 | 7.8 |
| | HHVD | 7.4 | 6.8 | < 0.1 | 14.3 | 5.1 |
| BDE-99 | RCDL | 23.3 | 17.9 | 4.2 | 77.1 | 18.7 |
| | RCDB | 19.5 | 14.5 | < 0.2 | 88.6 | 22.7 |
| | HHVD | 11.8 | 12.0 | 7.7 | 16.1 | 2.6 |
| BDE-153 | RCDL | 4.3 | 4.1 | < 0.2 | 7.3 | 1.8 |
| | RCDB | 4.8 | 4.0 | 1.4 | 14.7 | 3.6 |
| | HHVD | 2.5 | 2.9 | < 0.2 | 5.9 | 2.1 |
| $\Sigma_6$tri-hexa-BDEs | RCDL | 47.3 | 40.7 | 6.8 | 135 | 32.6 |
| | RCDB | 41.4 | 33.5 | 8.9 | 147 | 35.4 |
| | HHVD | 24.4 | 22.4 | 12.3 | 41.5 | 9.1 |
| BDE-183 | RCDL | 5.7 | 6.0 | < 0.2 | 11.3 | 3.4 |
| | RCDB | 2.4 | 2.8 | < 0.2 | 5.1 | 1.7 |
| | HHVD | 7.2 | 2.5 | < 0.2 | 61.2 | 17.1 |
| BDE-209 | RCDL | 2642 | 3066 | 466 | 4184 | 1354 |
| | RCDB | 2336 | 2232 | 1175 | 3944 | 780 |
| | HHVD | 2634 | 2462 | 1534 | 3779 | 802 |
| $\Sigma_8$PBDEs | RCDL | 2695 | 3112 | 474 | 4321 | 1363 |
| | RCDB | 2380 | 2272 | 1233 | 3985 | 775 |
| | HHVD | 2666 | 2519 | 1568 | 3795 | 797 |

**Table 6.4: Summary statistics for NBFR concentrations (ng/g) in RCDL, RCDB (researcher collected dust from the living room bedroom) and dust HHVD (household vacuum dust)**

| Target compound | Sampling method | Average | Median | Minimum | Maximum | Standard deviation |
|---|---|---|---|---|---|---|
| EH-TBB | RCDL | 6.9 | 6.4 | < 0.5 | 21.2 | 6.0 |
| | RCDB | 6.4 | 3.1 | < 0.5 | 24.2 | 7.9 |
| | HHVD | 4.9 | 3.9 | < 0.5 | 13.5 | 4.9 |
| BTBPE | RCDL | 11.0 | 11.2 | < 2.8 | 21.4 | 7.4 |
| | RCDB | 9.5 | 9.8 | < 2.8 | 15.8 | 4.9 |
| | HHVD | 11.2 | 8.0 | < 2.8 | 35.7 | 11.5 |
| BEH-TEBP | RCDL | 306 | 175 | 64 | 1299 | 348 |
| | RCDB | 339 | 131 | 43 | 1139 | 380 |
| | HHVD | 233 | 121 | 33 | 890 | 256 |
| DBDPE | RCDL | 155 | 87 | 14 | 679 | 184 |
| | RCDB | 91 | 76 | 11 | 236 | 65 |
| | HHVD | 152 | 85 | 16 | 575 | 170 |
| $\Sigma_5$NBFRs | RCDL | 479 | 394 | 127 | 1450 | 382 |
| | RCDB | 446 | 225 | 104 | 1412 | 420 |
| | HHVD | 402 | 272 | 129 | 1302 | 345 |

**Figure 6.2: Average concentrations (ng/g) of BFRs in RCDL, RCDB (researcher collected dust from living room and bedroom) and HHVD (household vacuum dust) (y error bars denote standard deviation)**

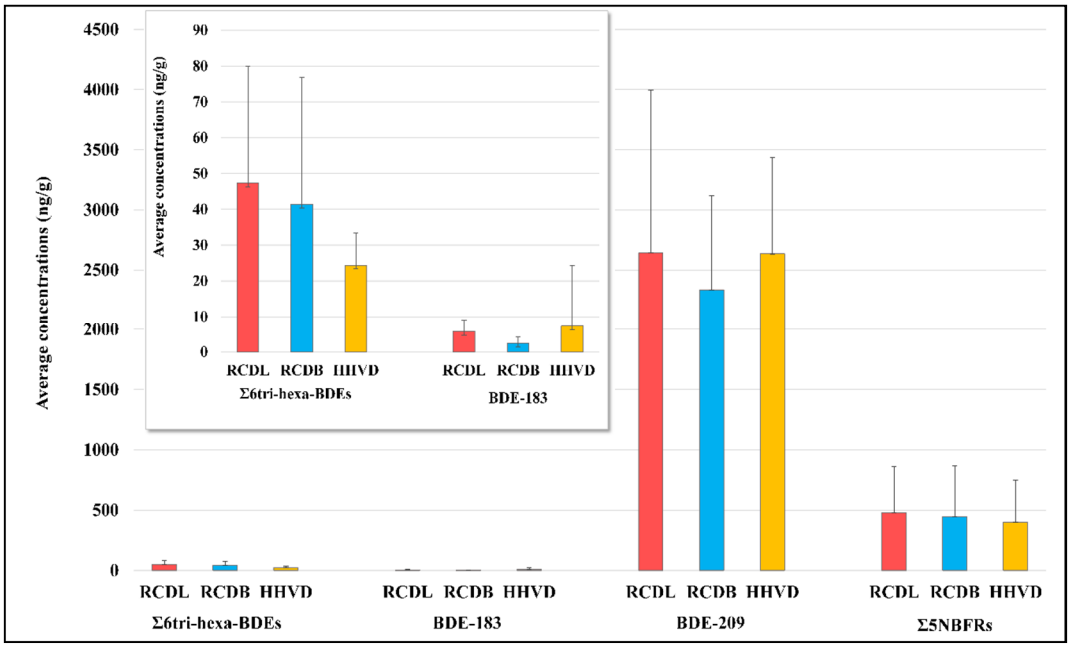



**Figure 6.3: Average concentrations (ng/g) of selected PBDEs in RCDL, RCDB (researcher collected dust from living room and bedroom) and HHVD (household vacuum dust) deviation (y error bars denote standard deviation)**

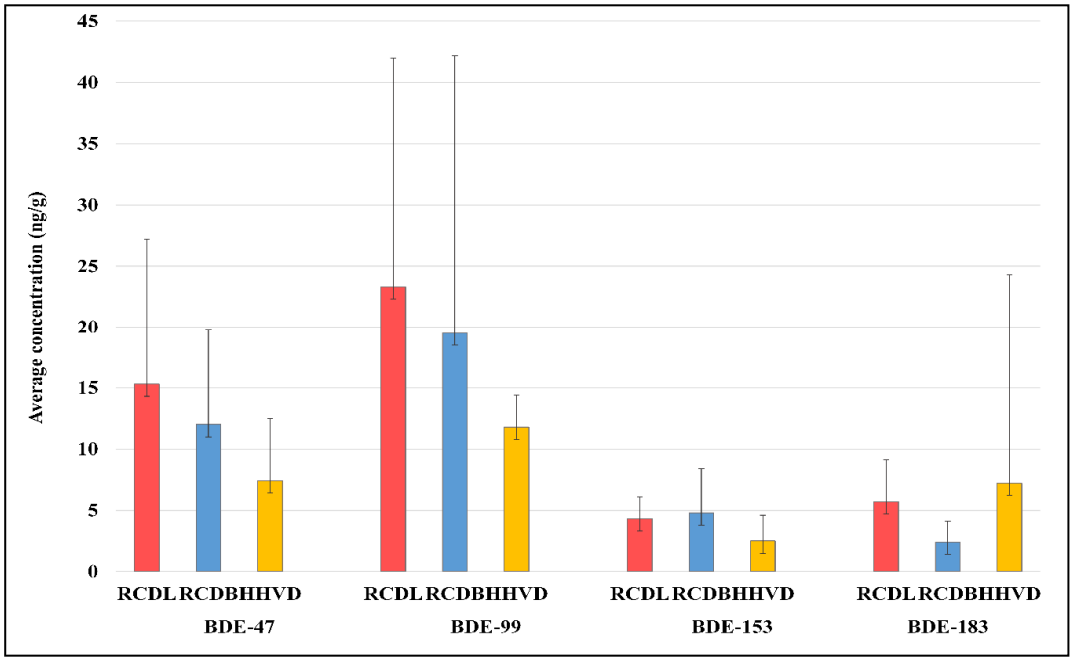
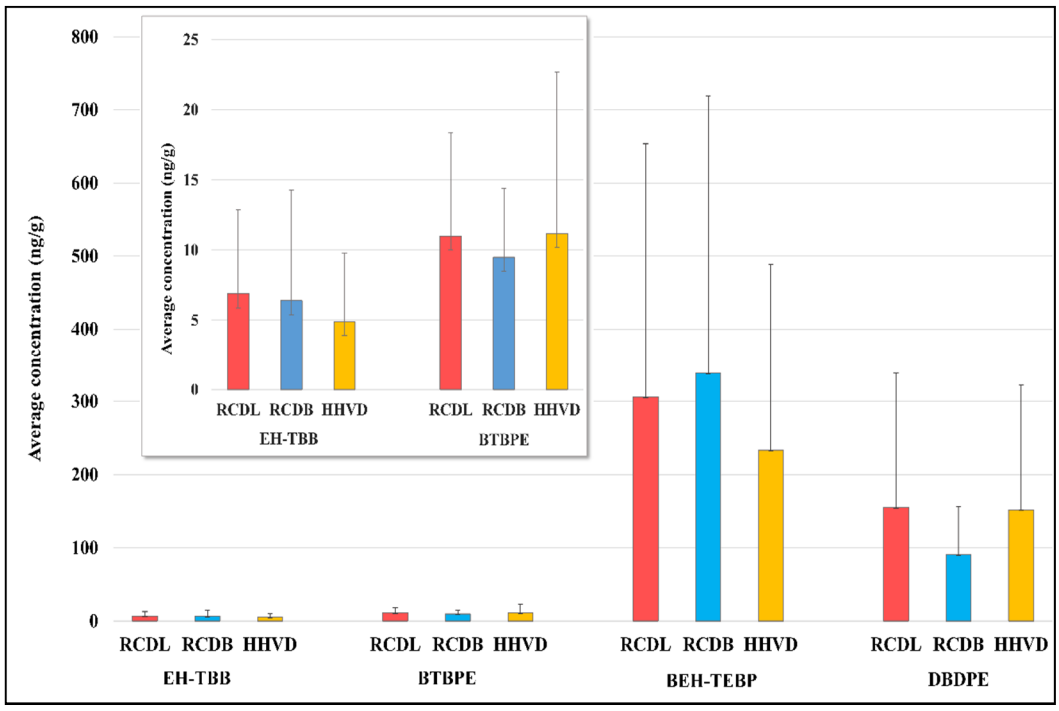


**Figure 6.4: Average concentrations (ng/g) of NBFRs in RCDL, RCDB (researcher collected dust from living room and bedroom) and HHVD (household vacuum dust) (y error bars denote standard deviation)**




### 6.3.3 Comparison of BFR concentrations in dust samples from two sampling methods

As evident from Tables 6.3 and 6.4, concentrations of BDE-47, BDE-99, BDE-153, $\Sigma_6$tri-hexa-BDEs and BEH-TEBP in researcher-collected dust from both living room (RCDL) and bedroom (RCDB) exceeded those in household vacuum dust (HHVD). In contrast, BDE-183 in HHVD was higher than RCDL and RCDB. In addition, BDE-209, BTBPE, and DBDPE concentrations in HHVD were only higher than in RCDB and they were comparable in both RCDL and HHVD. Table 6.5 lists the average concentration ratios RCDL/ HHVD and RCDB/ HHVD for BDE-47, BDE-99, BDE-153, BDE-BDE-183, BDE-209, EH-TBB, BEH-TEBP and DBDPE.

**Table 6.5: BFR average concentration ratios between researcher-collected dust from living room (RCDL) and bedroom (RCDB), and household vacuum dust (HHVD)**

| Target compound | RCDL/ HHVD | RCDB/ HHVD |
|---|---|---|
| BDE-47 | 2.1 | 1.6 |
| BDE-99 | 2.0 | 1.6 |
| BDE-153 | 1.7 | 1.9 |
| EH-TBB | 1.4 | 1.3 |
| BEH-TEBP | 1.3 | 1.5 |
| BDE-183 | 0.8 | 0.3 |
| BDE-209 | 1.0 | 0.9 |
| BTBPE | 1.0 | 0.8 |
| DBDPE | 1.0 | 0.6 |

To test any differences in mean BFR dust concentrations between the two collection methods (researcher-collected and household vacuum), and between the two researcher-collected rooms (living room and bedroom) one way repeated measures ANOVA was performed. After normality examination using the Shapiro–Wilk test, the skewed distribution data were transformed using the natural logarithm of concentrations (ng/g dw). The data showed, with the exceptions of $\Sigma_6$tri-hexa-BDEs, BDE-153, BDE-99 and to a moderate extent of BEH-TEBP, these differences were not statistically significant. $\Sigma_6$tri-hexa-BDEs and BDE-153 concentrations in researcher-collected dust exceeded significantly those in the household vacuum dust with *p* values of 0.012 and 0.038 for $\Sigma_6$tri-hexa-BDEs, and 0.025 and 0.016 for BDE-153 in RCDL and RCDB respectively. BDE-99 concentrations in RCDL exceeded significantly those in HHVD with a *p* value of 0.015. Moreover, BEH-TEBP concentrations in RCDL exceeded those in HHVD at a moderate level of significance ($p = 0.077$).

ANOVA tests revealed, with the exception of BDE-183, no significant differences ($p > 0.05$) in BFR concentrations between the living room and bedroom. With respect to BDE-183, concentrations in the living room exceeded significantly those in the bedroom with a *p* value of 0.001. Based on our results, Penta-BDE (represented by $\Sigma_6$tri-hexa-BDEs) and to a lesser extent BEH-TEBP displayed important differences between the two sampling methods, while

Deca-BDE (represented by BDE-209), Octa-BDE (represented by BDE-183), EH-TBB, BTBPE and DBDPE did not appear significantly impacted by the sampling method employed.

To date, there are few studies that have investigated the association between indoor dust sampling method and the concentration of pollutants. Early studies investigated different dust sampling methods of house dust, indicating that the HVS3 (high-volume small surface sampler) had the highest level of precision among different standardised vacuuming and wipe sampling methods (Sterling et al., 1999), due to the small particles that can be retained by the HVS3 (Lioy et al., 2002). A similar study in this area (Bai et al. 2003) reported that surface wipe sampling was the best method to measure accessible Pb from carpets for exposure assessment. In 2008, Clot et al., compared levels of pesticides, PAHs and PCBs in dust samples collected using HVS3 with corresponding household vacuum cleaner bag samples, and concluded that the household vacuum cleaner method was a viable alternative to the HVS3.

To our knowledge, only two studies (Allen et al., 2008; Björklund et al., 2012) have investigated comparisons of PBDE and HBCD concentrations in house dust collected via different sampling methods. This study is the first investigation of NBFR concentrations in dust samples collected using different sampling methods. In a comprehensive study of indoor dust from 20 homes in Boston, USA; Allen et al., (2008) compared concentrations of PBDEs in dust collected using household vacuum cleaner and researcher-collected (from living room and bedroom) methods. The study reported that Penta-BDE (ΣBDE-17, 28/33, 47, 49, 66, 75, 85/155, 99, 100, 183, 153 and 154) concentrations in researcher-collected dust samples exceeded significantly those in the household vacuum dust in both living room ($p$ = 0.001) and bedroom ($p$ = 0.002). In addition, the concentrations of Deca-BDE formulation congeners (BDE-206, 207, 208 and 209) in the researcher-collected dust from the living room exceeded significantly ($p$ = 0.02) those in the household vacuum dust, with such significant differences to the household vacuum dust not observed for bedroom researcher-collected samples. Moreover, the same study found no significant difference between Octa-BDE concentrations in dust obtained via the two sampling methods. With the exception of the concentrations of Deca-BDE formulation congeners in researcher-collected dust from the living room, our outcomes are consistent with the study of Allen et al. (2008), despite the differences in PBDE distribution profiles between the UK and USA, different sampling accessories (nylon sock

and cellulose extraction thimble), different vacuum cleaner brands and different dust particle size fractions (< 500 μm and < 250 μm).

Based on analysis of dust samples from 19 Swedish homes, Björklund et al., 2012, investigated the differences between PBDE and HBCD concentrations in samples collected via researcher-collected and household vacuum methods. The researcher-collected method employed involved collection of settled house dust from elevated surfaces (1 m above the floor). Concentrations of all targeted PBDE congeners (BDE-28, BDE-47, BDE-49, BDE-66, BDE-85, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-197, BDE-203, BDE-206, BDE-207, BDE-208, and BDE-209) detected in researcher-collected dust exceeded significantly ($P$ < 0.001- 0.003) those collected using the household vacuum method. The significant differences observed in this study (Björklund et al., 2012) between researcher-collected method and household vacuum method exceeded those observed both in our study and that of Allen et al. (2008). This implies that, in addition to the different sampling methods, different sampling surfaces (floor dust and elevated surface dust) exert an important influence on the findings of the Swedish study. This is consistent with findings reported in Chapters 3, 5, and 7, that BFR concentrations in elevated surface dust samples exceed significantly those in floor dust.

### 6.3.4 Correlation between dust sampling methods

Pearson correlation analysis was performed on log-transformed data to determine the relationship between BFR concentrations in household vacuum dust (HHVD) and researcher collected dust (RCD) from the living room (RCDL) and bedroom (RCDB). The strongest correlations observed between HHVD and RCD methods was for BEH-TEBP concentrations in the living room ($R$ = 0.793, $p$ = 0.002) and bedroom ($R$ = 0.883, $p$ = < 0.001). The same relationship was found for $\Sigma_6$tri-hexa-BDE concentrations ($R$ = 0.583, $p$ = 0.047) and ($R$ = 0.588, $p$ = 0.044), and DBDPE concentrations ($R$= 0.643, $p$ = 0.024) and ($R$ = 0.634, $p$ = 0.027) between HHVD and each of RCDL and RCDB respectively. In addition, concentrations of BDE-99 in HHVD were significantly ($R$ = 0.54, $p$ = 0.064) correlated with those in RCDL, but not with RCDB. Moreover, HHVD concentrations were moderately ($R$ = 0.532, $p$ = 0.075) associated with RCDL concentrations for BDE-209, and for EH-TBB ($R$ = 0.557, $p$ = 0.060) in RCDB. Appendix 6 lists the $R$ and $P$ values resulting from Pearson correlation analyses between HHVD and RCD for each of our target compounds. Figures 6.5,

6.6, 6.7 and 6.8 show scatter plots and Pearson correlation coefficients for obtained when plotting log-transformed concentrations of BDE-99, $\Sigma_6$tri-hexa-BDEs, BEH-TEBP and DBDPE in household vacuum dust against concentrations in both RCDL and RCDB respectively.

**Figure 6.5: Correlations between log-transformed BDE-99 concentrations in household vacuum dust and researcher-collected dust from the living room**

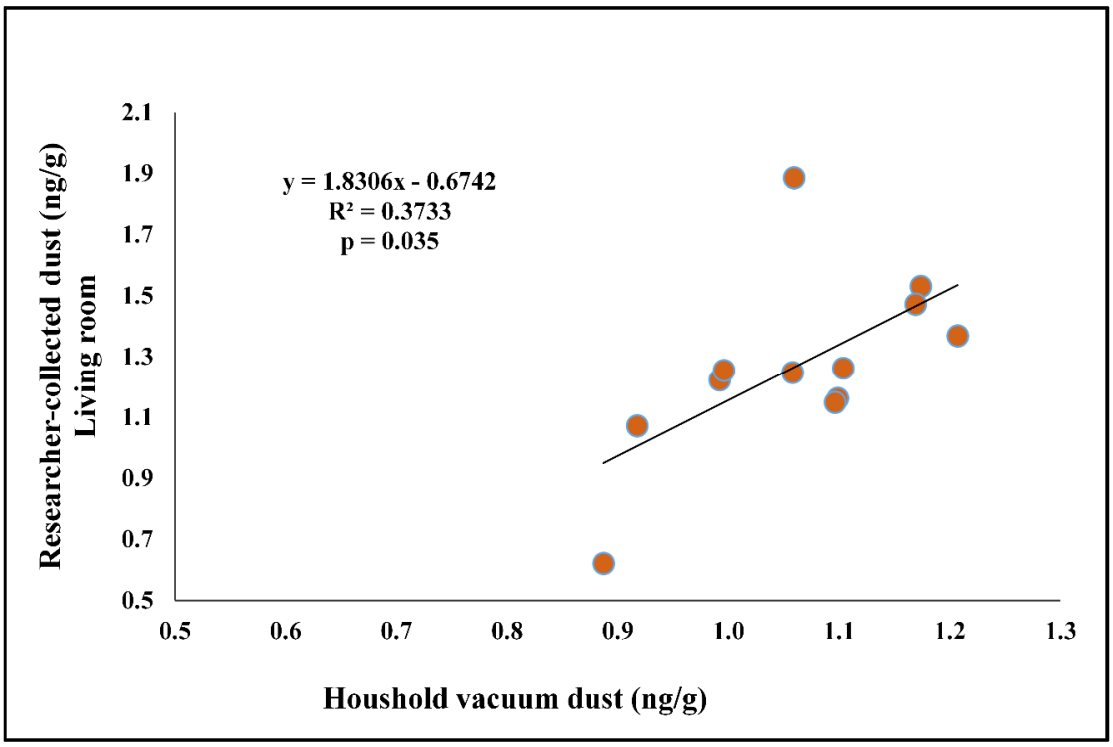


**Figure 6.6: Correlations between log-transformed $\Sigma_6$tri-hexa-BDEs concentrations in household vacuum dust and researcher-collected dust from: (a) the living room and (b) bedroom**

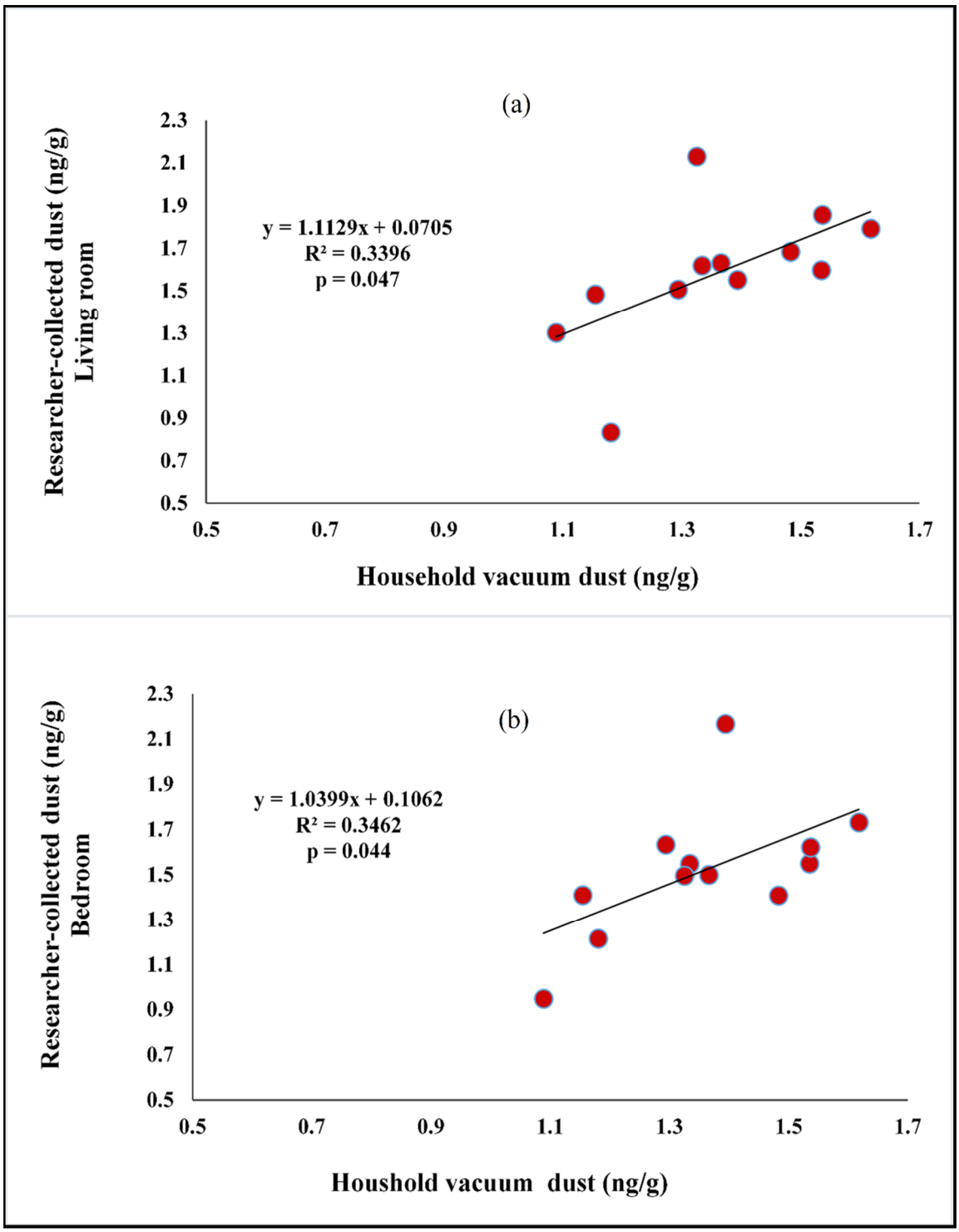


**Figure 6.7: Correlations between log-transformed concentrations of BEH-TEBP in household vacuum dust and researcher-collected dust from: (a) the living room and (b) bedroom**

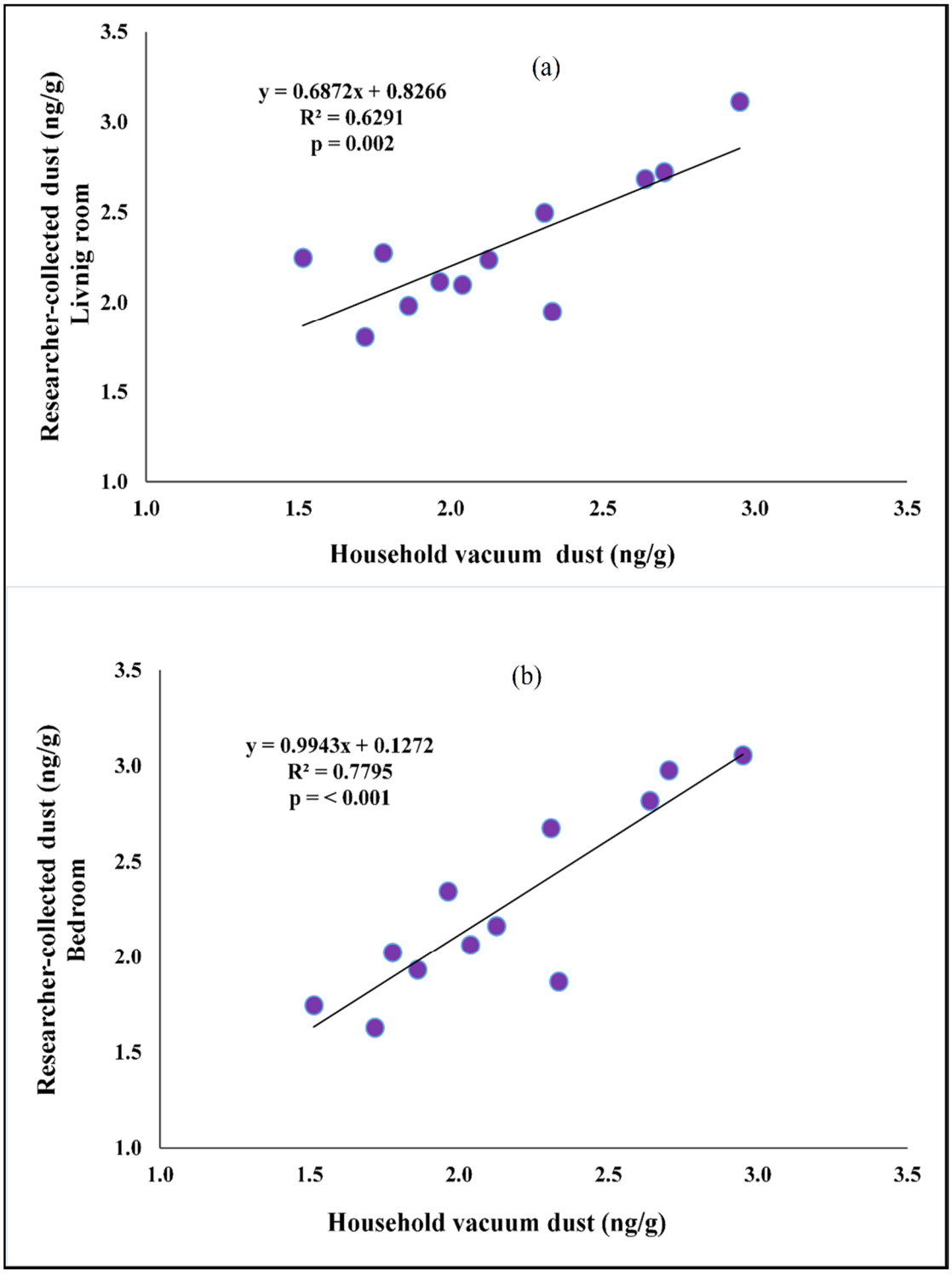
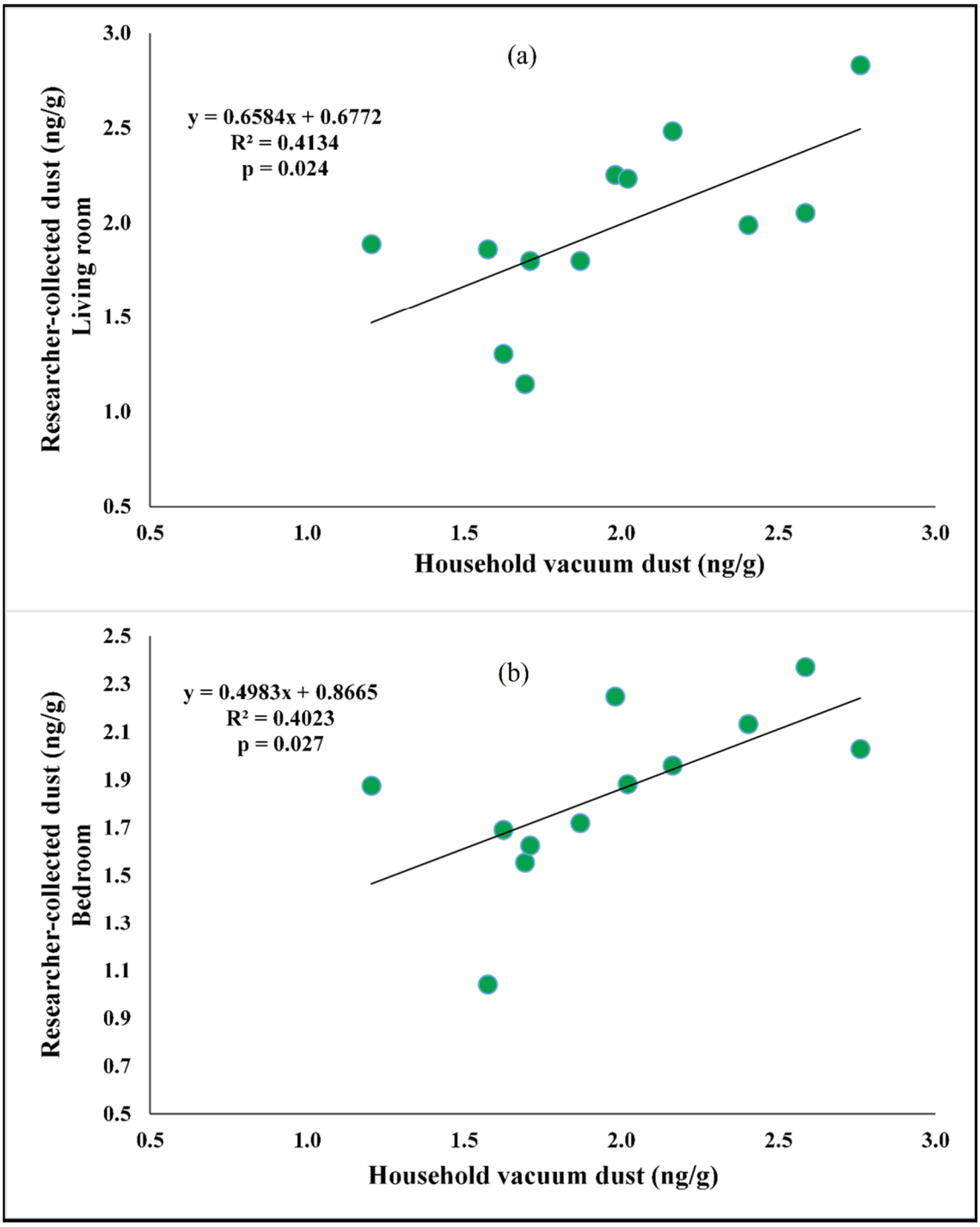


**Figure 6.8: Correlations between log-transformed concentrations of DBDPE in household vacuum dust and researcher-collected dust from: (a) the living room and (b) bedroom**



In general our findings revealed that BFR dust concentrations were highly correlated between the two sampling methods for BEH-TEBP, DBDPE, $\Sigma_6$tri-hexa-BDEs and BDE-99, and weakly correlated for BDE-209 and EH-TBB; while BDE-47, BDE-153, BDE-183 and BTBPE concentrations were not significantly correlated between researcher-collected and household vacuum dust. For PBDEs, with the exception of BDE-209, these findings are consistent with previous studies (Allen et. al 2008; Björklund et al., 2012). However, Björklund et al., (2012) concluded that, when a single high value of BDE-209 was removed from their data analysis, the correlation between concentrations obtained via the 2 dust collection methods was no longer significant (Björklund et al., 2012). The correlations observed for many (but not all) of our target BFRs indicates that HHVD and RCD from the living room/ bedroom are broadly (but not entirely) equivalent metrics of BFR contamination in indoor dust.

## 6.4 Sampling approach impact on human exposure assessments to BFRs

To evaluate to what extent that human exposure to our target contaminants via dust ingestion is affected by the choice of sampling approach, we compared the median concentration (for typical exposure) and 95$^{th}$ percentile (for high end exposure) in dust samples that collected in the two sampling approaches; researcher collected from the living room and bedroom (RCDL and RCDB) and house hold vacuum (HHVD) approaches. The comparison data observed that the sampling method impact on BDE-99 and Σtri-hexa-BDEs was more important than on the other target compounds. BDE-99 and Σtri-hexa-BDEs in RCD (researcher-collected dust) exceeded substantially HHVD by factors ranged between 1.2- 3.5. This implies that estimated exposure assessments based on analysis of these compounds in HHVD may be underestimated, particularly in high-end exposure assessments. BEH-TEBP estimated exposure assessments based on analysis of RCD exceeded those of HHVD by factors of 1.1- 1.5. With the exception of the DBDPE concentrations in RCDB, almost comparable results were obtained for BDE-209 and DBDBE concentrations collected via the two sampling methods. DBDPE concentrations in HHVD samples exceeded those in RCDB samples by factors of 1.1 and 2.3 for median and 95$^{th}$ percentile concentrations respectively, which implies that analysing HHVD may overestimate exposure to DBDPE. Table 6.6 illustrates RCDL/HHVD and RCDB/HHVD median and 95$^{th}$ percentile concentration ratios for BDE-99, Σtri-hexa-BDEs, BDE-209, BEH-TEBP and DBDPE, which illustrate the impact of sampling method on typical and high-end exposure assessments. Appendix 7

compares exposure assessments for these BFRs based on ingestion of dust collected with the two different sampling methods under three scenarios for adults and toddlers.

**Table 6.6: Median and 95th percentile concentration ratios of BDE-99, $\Sigma_6$tri-hexa-BDEs, BDE-209 and DBDPE between researcher collected-dust from the living room and bedroom (RCDL and RCDB) and household vacuum dust**

| Compound | Sampling approach | Median | 95$^{th}$ percentile |
|---|---|---|---|
| BDE-99 | RCDL/HHVD | 1.5 | 3.5 |
| | RCDB/HHVD | 1.2 | 3.4 |
| $\Sigma_6$tri-hexa-BDEs | RCDL/HHVD | 1.8 | 2.7 |
| | RCDB/HHVD | 1.5 | 2.6 |
| BDE-209 | RCDL/HHVD | 1.2 | 1.1 |
| | RCDB/HHVD | 0.9 | 1.0 |
| BEH-TEBP | RCDL/HHVD | 1.4 | 1.3 |
| | RCDB/HHVD | 1.1 | 1.5 |
| DBDPE | RCDL/HHVD | 1.0 | 1.0 |
| | RCDB/HHVD | 0.9 | 0.4 |

A few studies use the term “biologically relevant” dust samples – i.e. which dust sampling method provides dust samples most relevant to human body burdens. Unless concomitant dust and body burden measurements are made, it is impossible to tell which dust sampling method is more biologically relevant (Allen et al., 2008). Due to the lack of a universally agreed standard sampling method, Harrad et al., (2010b) concluded that the best approach is to provide full details of the dust sampling method used when reporting results. In general, depending on the study purpose, the advantages and disadvantages of each sampling method should be identified. Details about advantages and disadvantages of each approach are provided in Chapter 1, section 1.8.2.4.

## 6.5 The relationship between the BFR dust concentration and dust loading

Human exposure to BFRs and other related compounds via indoor dust ingestion have been assessed depending on a "default" rate ingestion regardless of dust loading (g dust per $m^2$ floor surface) of the microenvironment (Harrad et al., 2008a). Under certain conditions, Harrad et al. 2008a; 2009; Muenhor and Harrad, 2012 hypothesised that BFR concentrations will be "diluted" at high dust loading. These conditions assume that the BFR emission rate will be constant during the emission period, in addition, the source of BFR and indoor dust are independent. While there are no data addressing the relationship between BFR dust loading ($g/m^2$) and dust concentration (ng/g), our data on the temporal variability in Chapter 4, from Home 1, Home 2, and Home 3 offer an opportunity to evaluate this relationship. These data were obtained from samples taken from the same two floor areas every month for nine months from the nine rooms studied (with exclusion of the H1R3F2 area as the sampling was conducted only for four months due to the personal reasons related to the occupants). Overall 17 floor areas were investigated to test the relationship between dust loading and BFR concentrations (Figures 3.1, 3.2 and 3.3, Chapter 3).

Due to the above mentioned dilution factor, a plot of Log (dust loading) versus Log (BFR concentration is expected to be linear with negative slope. Pearson correlation was applied to test the relationship between BFR (BDE-99, $\Sigma_7$tri-hepta-BDE, BDE-209 and BEH-TEBP and DBDPE (with detection frequencies > 90%) concentrations and dust loading from the seventeen individual areas. This revealed significant negative correlations ($p < 0.05$) between BFR concentrations and dust loading in two floor sample series and positive correlation in one floor series area. Significant negative relationship was observed between log concentrations of BDE-99 ($R = 0.675$, $p = 0.046$) and $\Sigma_7$tri-hepta-BDEs ($R = 0.760$, $p = 0.018$) and log dust loading for sample series H2R2F2 (Figure 3.2 Chapter 3). The same relationship was observed between log concentrations of BEH-TEBP ($R = 0.749$, $p = 0.020$) and log (dust loading) in sample series H3R2F2 (Figure 3.3, Chapter 3). In one case only, a moderate positive correlation was found between log concentration of DBDPE ($R = 0.664$, $p = 0.051$) and log dust loading in series H3R1F2 (Figure 3.3, Chapter 3). No significant correlation was observed ($p > 0.05$) for the rest of our investigated compounds. Tables 6.7, 6.8 and 6.9 summarise the dust loading ($g/m^2$) and temporal variability in concentrations of the target BFRs in ng/g dust samples taken from H2R2F2, H3R2F2 and H3R1F2 areas, along with relative standard deviation (RSD). Figures 6.9, 6.10, 6.11 and 6.112 show scatter plots and

Pearson correlation coefficients obtained when plotting log-transformed concentrations of BDE-99, $\Sigma_7$tri-hepta-BDEs BEH-TEBP and DBDPE and log dust loading respectively.

**Table 6.7: Dust loading (g/m²) and temporal variability in BFR concentrations (ng/g) in Home 2 (H2R2F2)**

| Sampling time | Dust loading (g/m²) | BDE-99 | Σtri-hepta-BDEs | BDE-209 | BEH-TEBP | DBDPE |
|---|---|---|---|---|---|---|
| May-13 | 0.329 | 30.2 | 61.4 | 2253 | 105 | 106 |
| Jun-13 | 0.323 | 35.3 | 66.1 | 3277 | 267 | 174 |
| Sep-13 | 0.208 | 43.1 | 81.1 | 2180 | 72 | 57 |
| Oct-13 | 0.239 | 41.1 | 81.8 | 1955 | 91 | 156 |
| Nov-13 | 0.224 | 44.8 | 77.8 | 3340 | 94 | 226 |
| Dec-13 | 0.421 | 34.1 | 60.6 | 2552 | 122 | 171 |
| Jan-14 | 0.313 | 16 | 31.5 | 3674 | 90 | 58 |
| Feb-14 | 0.312 | 24.7 | 54.7 | 3499 | 88 | 73 |
| Mar-14 | 0.396 | 20.7 | 43.5 | 3796 | 72 | 31 |
| RSD | 24 | 32 | 28 | 24 | 54 | 57 |

**Table 6.8: Dust loading (g/m²) and temporal variability in BFR concentrations (ng/g) in Home 3 (H3R2F2)**

| Sampling time | Dust loading (g/m²) | Σtri-hepta-BDEs | BDE-209 | BEH-TEBP | DBDPE |
|---|---|---|---|---|---|
| May-13 | 0.253 | 39.2 | 3186 | 2333 | 84 |
| Jun-13 | 0.24 | 17.7 | 4459 | 4833 | 11 |
| Sep-13 | 0.639 | 20.6 | 4365 | 3251 | 15 |
| Oct-13 | 0.493 | 32.7 | 4165 | 2894 | 19 |
| Nov-13 | 0.557 | 6.7 | 4035 | 1889 | 152 |
| Dec-13 | 0.498 | 31.7 | 4251 | 1858 | 125 |
| Jan-14 | 0.432 | 62.8 | 4292 | 1902 | 97 |
| Feb-14 | 1.03 | 58.4 | 4423 | 1528 | 95 |
| Mar-14 | 1.2 | 51.3 | 3987 | 765 | 20 |
| RSD | 55 | 54 | 9 | 50 | 78 |

**Table 6.9: Dust loading (g/m²) and temporal variability in BFR concentrations (ng/g) in Home 3 (H3R1F2)**

| Sampling time | Dust loading (g/m²) | Σtri-hepta-BDEs | BDE-209 | BEH-TEBP | DBDPE |
|---|---|---|---|---|---|
| May-13 | 0.2 | 49.7 | 3243 | 1576 | 33 |
| Jun-13 | 0.143 | 57.6 | 4452 | 1336 | 24 |
| Sep-13 | 0.353 | 24.6 | 3690 | 1567 | 35 |
| Oct-13 | 0.045 | 19.9 | 8901 | 821 | 6 |
| Nov-13 | 2.155 | 4.6 | 3331 | 309 | 101 |
| Dec-13 | 1.276 | 17.0 | 3850 | 853 | 60 |
| Jan-14 | 0.368 | 38.1 | 3828 | 583 | 42 |
| Feb-14 | 1.462 | 14.0 | 4237 | 691 | 22 |
| Mar-14 | 0.8 | 46.2 | 4096 | 603 | 13 |
| RSD | 96 | 61 | 39 | 49 | 77 |

**Figure 6.9: Negative relationship between log {dust loading ($g/m^2$)} and log concentrations (ng/g) of BDE-99 in house dust from H2R2F2**

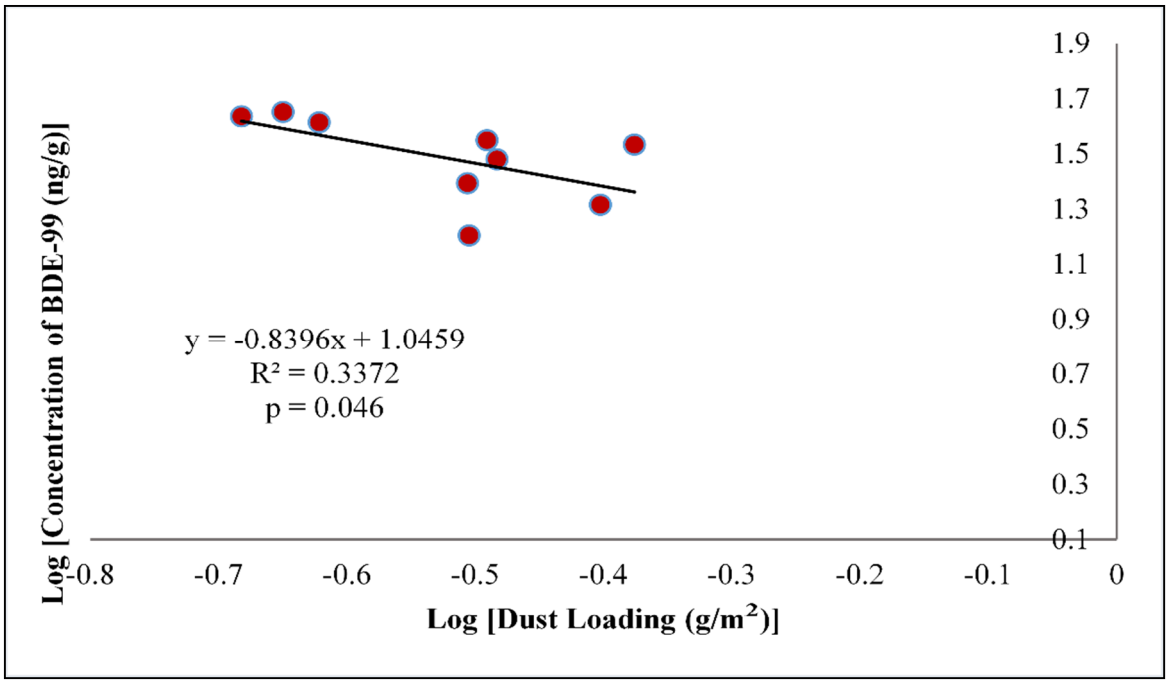



**Figure 6.10: Negative relationship between log {dust loading ($g/m^2$)} and log concentrations (ng/g) of $\Sigma_7$tri-hepta-BDEs in house dust from H2R2F2**

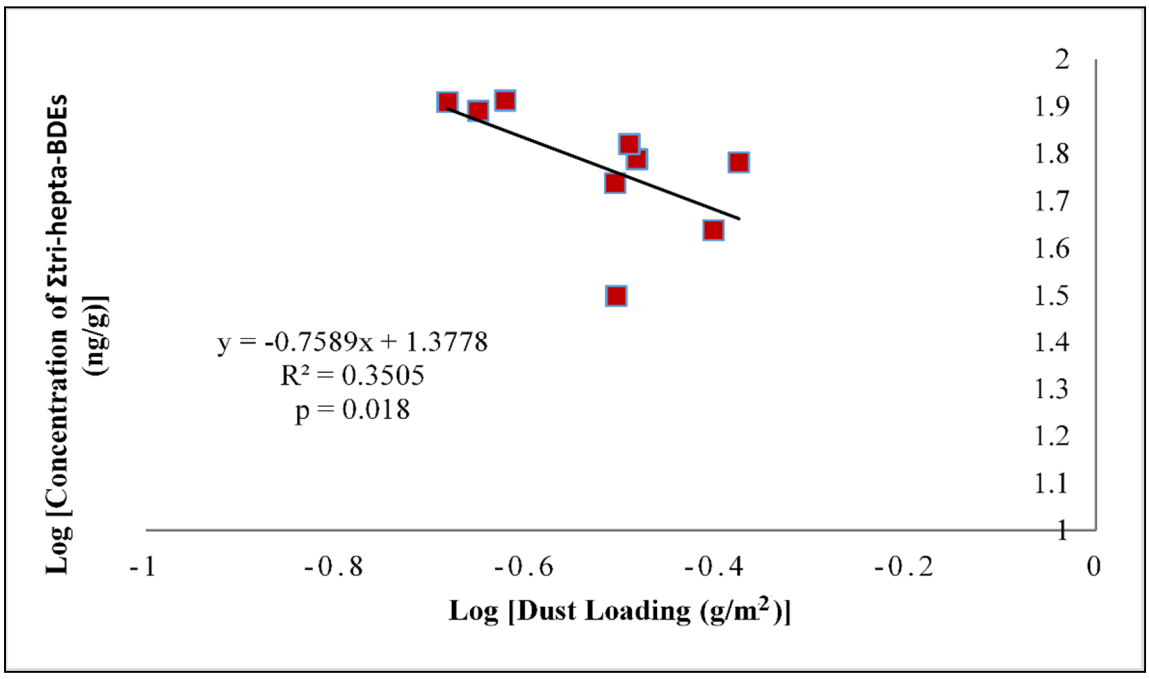


**Figure 6.11: Negative relationship between log {dust loading (g/m$^2$)} and log concentrations (ng/g) of BEH-TEBP in house dust from H3R2F2**

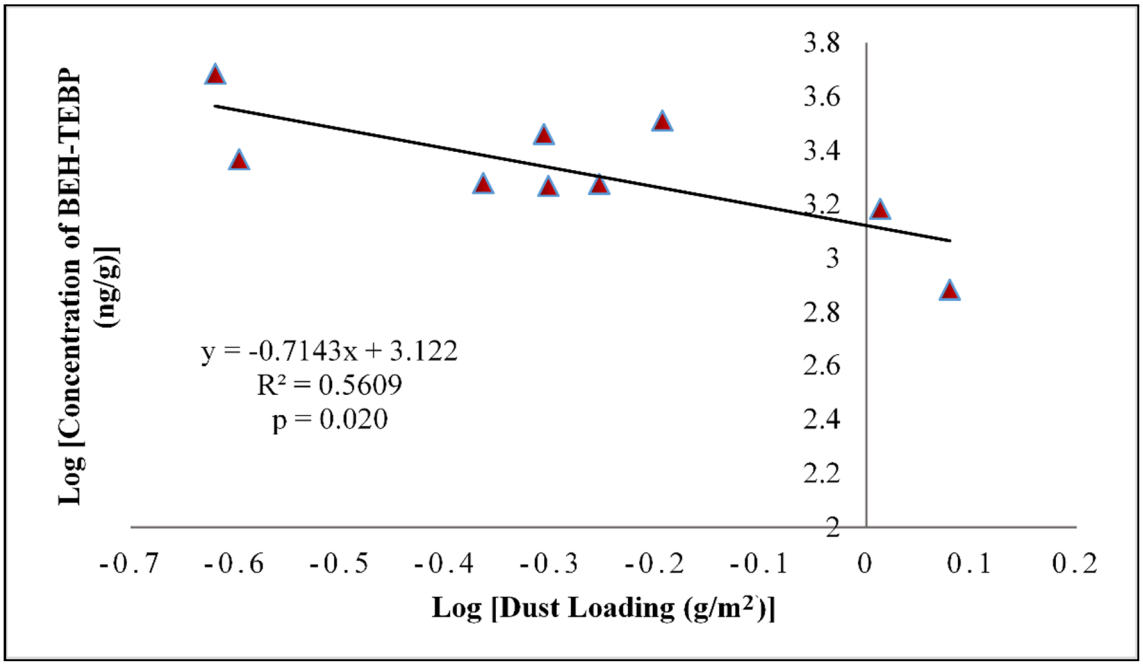
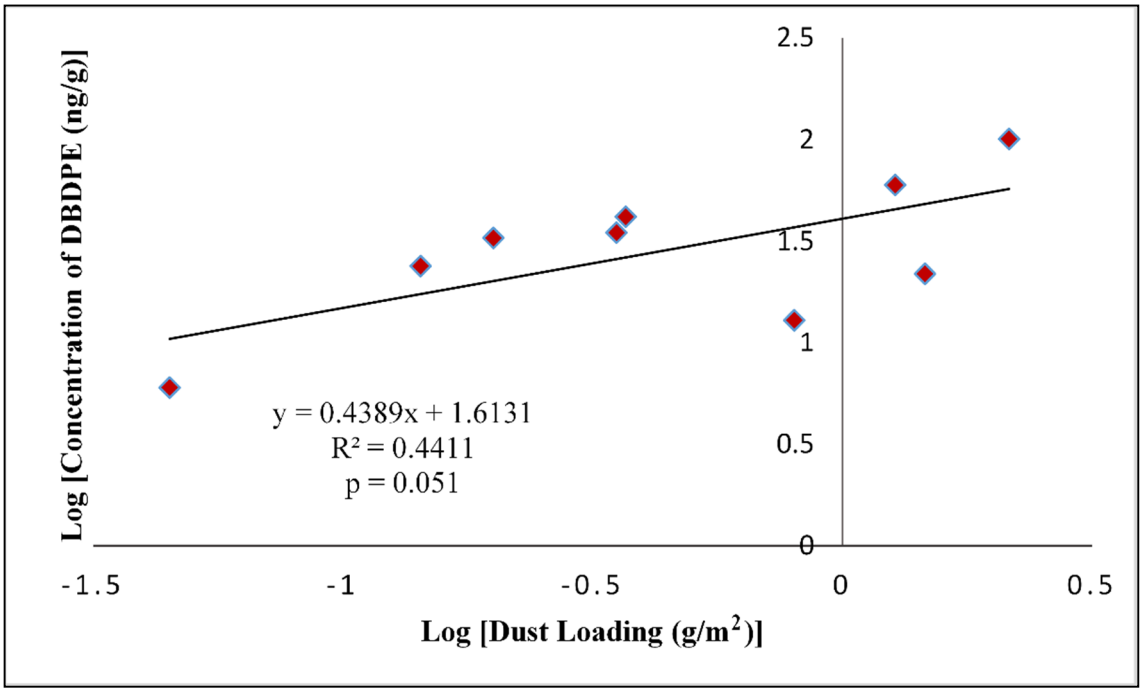



**Figure 6.12: Positive relationship between log {dust loading (g/m$^2$)} and log concentrations (ng/g) of DBDPE in house dust from H3R1F2**



These negative correlation results observed in the main bedrooms of Home 2 and Home 3 are consistent with the hypothesis that dilution of concentrations of BDE-99, $\Sigma_7$tri-hepta-BDEs and BEH-TEBP as dust loading increased. In addition, this indicates that the sources of the mentioned compounds and indoor dust are independent (i.e. volatilisation followed by deposition to dust). On the other hand, the positive correlation between DBDPE concentration and dust loading in the living room of Home 3, indicates that the source(s) of DBDPE and indoor dust are the same, which implies that physical transfer of DBDPE via abrasion from products in the form of particles or/and fibres. In general, our results are consisted with those of previous studies (Harrrad et al., 2008a; 2009; Muenhor and Harrad, 2012). In a study in the UK, Harrad et al., 2008a reported that, in one room, a significant negative correlation ($p < 0.05$) was observed between concentrations of BDE-47, -99 and -153 and dust loading. In another study, the same authors (Harrad et al., 2009) found the same relationship ($R = 0.68$; $p < 0.05$) between ΣHBCDs and dust loading implying dilution occurs at higher dust loadings.

## 6.6 Conclusions

The chapter primarily examines the effect of indoor dust sampling method on PBDE and NBFR concentrations and consequent human exposure. In general, our outcomes suggest that BFR concentrations in HHVD (household vacuum dust) were lower than those in RCD (researcher collected dust) from both living rooms and bedrooms, and significantly higher for BDE-99, BDE-153, $\Sigma_6$tri-hexa-BDEs and –to some extent- BEH-TEBP. This might be due to volatilisation of BFRs as a result of the long residence times of dust in the household vacuum. In addition, small particles may have been lost through collecting and transferring processes from the vacuum bag. Our results in Chapter 5 revealed that lower brominated BFRs are significantly higher in the finest particle size fractions. Our findings in this chapter indicate that exposure assessments using HHVD may be underestimated for $\Sigma_6$tri-hexa-BDEs and BEH-TEBP, which suggest that this approach is not suitable to represent human exposure assessments to these compounds, however, it could be a viable alternative to RCD for higher brominated BFRs such as BDE-209.

In this chapter, we identified dilution of BFRs at high dust loading to be occurring in a few instances. In three out of seventeen individual floor areas, BDE-99, $\Sigma_6$tri-hepta-BDEs and BEH-TEBP concentrations decreased as dust loading increased, suggesting that the source of

these compounds and indoor dust are independent. On the other hand, in one sampled area, positive correlation between DBDPE concentration and dust loading revealed that the sources of both dust and DBDPE are dependent, which suggested that DBDPE released to the indoor dust via abrasion of fibres or particles from treated material.

Future studies are recommended to examine the particle size distribution pattern of BFR concentrations in indoor dust obtained via the two sampling methods, to test the hypothesis that a greater proportion of fine particles in RCD account for the higher BFR concentrations observed in such dust compared to HHVD. This is because the same compounds (BDE-99, BDE-153, $\Sigma_6$tri-hexa-BDEs and BEH-TEBP) that were significantly elevated in researcher collected compared to household vacuum collected dust, are also significantly higher in the finest particle size fractions of indoor dust (Chapter 5).

# CHAPTER 7

# POLYBROMINATED DIPHENYL ETHERS AND "NOVEL" BROMINATED FLAME RETARDANTS IN FLOOR AND ELEVATED SURFACE HOUSE DUST FROM IRAQ: IMPLICATIONS FOR HUMAN EXPOSURE ASSESSMENT

This chapter contains sections of text taken verbatim from the following publication: "L. S. Al-Omran, S. Harrad. "Polybrominated diphenyl ethers and "novel" brominated flame retardants in floor and elevated surface house dust from Iraq: Implications for human exposure assessment", *Emerging Contaminants*, 2, 7-13 (2016)."

## 7.1 Summary

Concentrations of PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209) and NBFRs (PBEB, EH-TBB, BTBPE, BEH-TEBP, and DBDPE) were measured in 36 indoor dust samples from the living areas of 18 homes in Basrah, Iraq. To evaluate the implications for human exposure, elevated surface dust (ESD) present on surfaces like tables, shelves and chairs, and floor dust (FD) were collected at the same time. This is the first report of contamination of the Iraqi environment with these chemicals.

The detection frequencies of BFRs ranged from 44% to 100%. BDE-209 was the predominated compound with average concentrations of 1160 and 762 ng/g, followed by DBDPE and BEH-TEBP with average concentrations of 173 and 129 ng/g for DBDPE, and 125 and 99.5 ng/g for BEH-TEBP in ESD and FD respectively. The average concentrations of the rest of our target compounds were found between 0.14 ng/g for PBEB in floor dust and 18.5 ng/g for BDE-99 in elevated surface dust. The PBDE contamination pattern in our samples suggests that use in Iraq of the Deca-BDE formulation, exceeds substantially that of Penta-BDE, but that use of the Octa-BDE formulation has been higher in Iraq than in some other regions.

A paired t-test comparison was applied to test the hypothesis that concentrations of PBDEs and selected NBFRs in dust from elevated surfaces will exceed significantly those in floor dust from the same microenvironment. The t-test outcomes revealed that BDE-28, BDE-99,

BDE-209, PBEB, BEH-TEBP and DBDPE concentrations in elevated surface dust exceeded significantly ($p < 0.05$) those in floor dust from the same living room. The *p* values were 0.047, 0.014, 0.002, 0.003, 0.036, and 0.031 for BDE-28, BDE-99, BDE-209, PBEB, BEH-TEBP, respectively.

Total organic carbon content (TOC) was measured to investigate whether any differences in BFR concentrations between ESD and FD could be attributed to differences in the TOC content. This indicated that the differences in organic carbon cannot explain the higher concentrations of some BFRs in elevated surface compared to floor dust. A paired t-test comparison of concentrations of BFRs normalised to the TOC content of both ESD and FD revealed that BDE-99, BDE-209, PBEB, BEH-TEBP, and DBDPE in ESD exceeded significantly those in FD, with *p* values of 0.028, 0.001, 0.015, 0.049 and 0.003 respectively.

To evaluate whether differences in dust particle size distribution between ESD and FD could account for the differences in BFR concentrations between the two dust types, the mass of particles present in two size fractions (125-250 and < 125 µm) was measured in both ESD and FD. Results showed significantly ($p < 0.05$) higher proportions of particles < 125 µm in ESD and of particles 125- 250 µm in FD. This suggests that the greater relative abundance of finer particles in ESD is the cause of the elevated BFRs in such dust compared to FD.

To our knowledge, this is the first study to investigate both elevated surface dust and floor dust in the context of the implications for human exposure assessment. Given our observed differences between BFR concentrations in ESD and FD, we believe that previous studies that base estimates of adult exposure via dust ingestion on floor dust only, may underestimate exposure. Such underestimation is less likely for toddlers who are more likely to ingest floor dust. Concentrations of PBDEs and NBFRs in indoor dust from Basrah, Iraq are at the lower end of those reported elsewhere. Reassuringly, our estimates of exposure to these contaminants via dust ingestion for the Iraqi population fall well below the relevant health-based limit values.

## 7.2 Sampling and sample preparation

From urban houses in Basrah province, South Iraq, 2 dust samples were collected from each of 18 houses, between July and August 2013. In each house, one sample was collected from the living area floor (referred to here as floor dust – FD), with a second sample collected that comprised settled dust from elevated surfaces in the same living area such as tables, shelves, bookcases (referred to here as elevated surface dust – ESD). Floor dust and elevated surface dust samples were collected according to the sampling procedure described in Chapter 2, section 2.3. At the time of sample collection, information on potential influences on BFR contamination such as: the number and type of putative sources like electronic devices, foam-filled furniture and floor material, ventilation system, house cleaning method, occupants and time spent in the living area was recorded on the questionnaire shown in Appendix 1. It was noticed that the Iraqi indoor dust loading was higher and was of a sandy texture compared with UK indoor dust. Samples were subsequently transferred to Birmingham, UK, for sieving and analysis. Prior to analysis, all dust samples were passed through a pre-cleaned, n-hexane rinsed 250 μm mesh testing sieve, covered with the lid and shaken for 2-4 min. Sieved samples were stored in clean, n-hexane rinsed glass jars and stored at 4 ˚C until analysis. For human exposure assessments, this study employed a 250 μm mesh sieve for two reasons: (1) evidence that concentrations of chemicals like BFRs vary according to particle size (Wei et al., 2009; Mercier et al., 2011; Cao al; 2013) and (2) studies that suggest strongly that particle adherence to human skin falls off markedly at diameters < 250 μm (Que Hee et al., 1985; Edwards and Lioy 1999; USEPA, 2000; 2003; Yamamoto et al., 2006)

## 7.3 Determination of organic carbon content in dust

In 12 homes, sufficient dust was available after BFR analysis to permit determination of total organic carbon (TOC) in both ESD and FD. To achieve this, approximately 20 mg of dust was weighed into 8 by 5 mm tin capsules using a Sartorious (Model MC5, Sartorious AG, Germany) microbalance. These samples were run through a 2000 Elemental Analyser (Thermo Fisher Scientific, Netherlands), using EDTA as a standard. Additional standards were run every 15 dust samples to check for machine drift. Organic carbon content measurements in this study were conducted at the University of Exeter, College of Life and Environmental Sciences.

## 7.4 Analytical method

With the exception of the GC-MS analysis conditions, the methodology followed in this study is identical to that described in Chapter 2, and which was used for analysis of UK dust samples in Chapters 3, 4, 5 and 6. In this study, the MS was operated in ECNI mode for determination of BDE-209 and all target NBFRs (except PBEB), and in EI mode for determination of other PBDEs and PBEB. Information about the GC/EI-MS analysis parameters, selected ion monitoring (SIM), and internal standard (IS) recoveries related to analysis of PBEB, BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154 and BDE-183 are provided in this chapter, while the GC/ ECNI-MS details for the rest of our target compounds are described in Chapter 2. Table 7.1 lists the GC/EI-MS parameters.

**Table 7.1: Parameters for the GC/EI-MS method**

| | | | | |
|---|---|---|---|---|
| **Oven Method** | - | Rate (°C/min) | Temperature (°C) | Hold Time (min) |
| | Initial | - | 110 | 2.0 |
| | 1 | 30 | 180 | 0.0 |
| | 2 | 20 | 260 | 0.0 |
| | 3 | 10 | 305 | 19.0 |
| **PTV Method** | Inlet temperature | | 92 ˚C | |
| | Split flow | | 50.0 Ml/min | |
| | Splitless time | | 1.0 min | |
| | Purge flow | | 5.0 Ml/min | |
| | Carrier mode | | Constant | |
| | Carrier flow | | 1.2 Ml/min | |
| | Gas saver flow | | 20.0 Ml/min | |
| | Gas saver time | | 5 min | |
| | Transfer Rate | | 5 min | |
| | Transfer Temperature | | 325 °C | |
| | Transfer time | | 20 min | |
| **MS Method** | Electron Lens Voltage | | 30 V | |
| | Emission Current | | 35 Ma | |
| | MS Transfer Line | | 280 °C | |
| | Ion Source Temperature | | 250 °C | |

$^{13}$C BDE-47 was used as a surrogate standard for quantification of BDE-28, BDE-47 and PBEB, $^{13}$C BDE-99 was used to quantify BDE-99 and BDE-100, while $^{13}$C BDE-153 was used for BDE-153, BDE-154 and BDE-183. Table 7.2 lists selected ion monitoring (SIM) (*m/z*) for the EI-MS instrumental method with internal standard recoveries for this method given in Table 7.3.

**Table 7.2: Ions monitored (m/z) in the EI Instrumental method.**

| Compound | Quantitative (m/z) | Qualitative (m/z) |
|---|---|---|
| BDE-28 | 405.8 | 407.8 |
| PBEB | 484.6 | 486.6 |
| BDE-47 | 483.5 | 485.5 |
| $^{13}$C-BDE-47 | 495.7 | 497.7 |
| BDE-100 | 403.7 | 405.7 |
| BDE-99 | 403.7 | 405.7 |
| $^{13}$C-BDE-99 | 415.7 | 417.7 |
| BDE-154 | 483.7 | 485.7 |
| BDE-153 | 483.7 | 485.7 |
| $^{13}$C-BDE-153 | 495.7 | 497.7 |
| BDE-183 | 561.6 | 563.6 |

**Table 7.3: Internal standard (IS) recoveries for matrix spike and dust samples**

| IS | Average recovery % (SD) in matrix spike (n=7) | Average recovery % (SD) in dust sample |
|---|---|---|
| $^{13}$C BDE-47 | 117.6 (16.8) | 101.3 (12.3) |
| $^{13}$C BDE-99 | 108.8 (9.7) | 96.7 (11.8) |
| $^{13}$C BDE-153 | 102.6 (14.3) | 94.2 (11.9) |

## 7.5 Results and discussion

### 7.5.1 Detection frequencies and the relationship between BFRs in house dust from Iraq

In the 36 Iraqi dust samples, the detection frequency of PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209) and NBFRs (PBEB, EH-TBB, BTBPE, BEH-TEBP, and DBDPE) ranged from 44% to 100%. The detection frequency of BDE-209 and DBDPE were 100% in both elevated surface dust (ESD) and floor dust (FD) samples, followed by BEH-TEBP, 100% and 89% in ESD and FD respectively. The lowest detection frequencies (44%) were found in BDE-28 and PEBE in floor dust samples. Table 7.4 lists the detection frequency of PBDEs and NBFRs in elevated surface and floor dust samples.

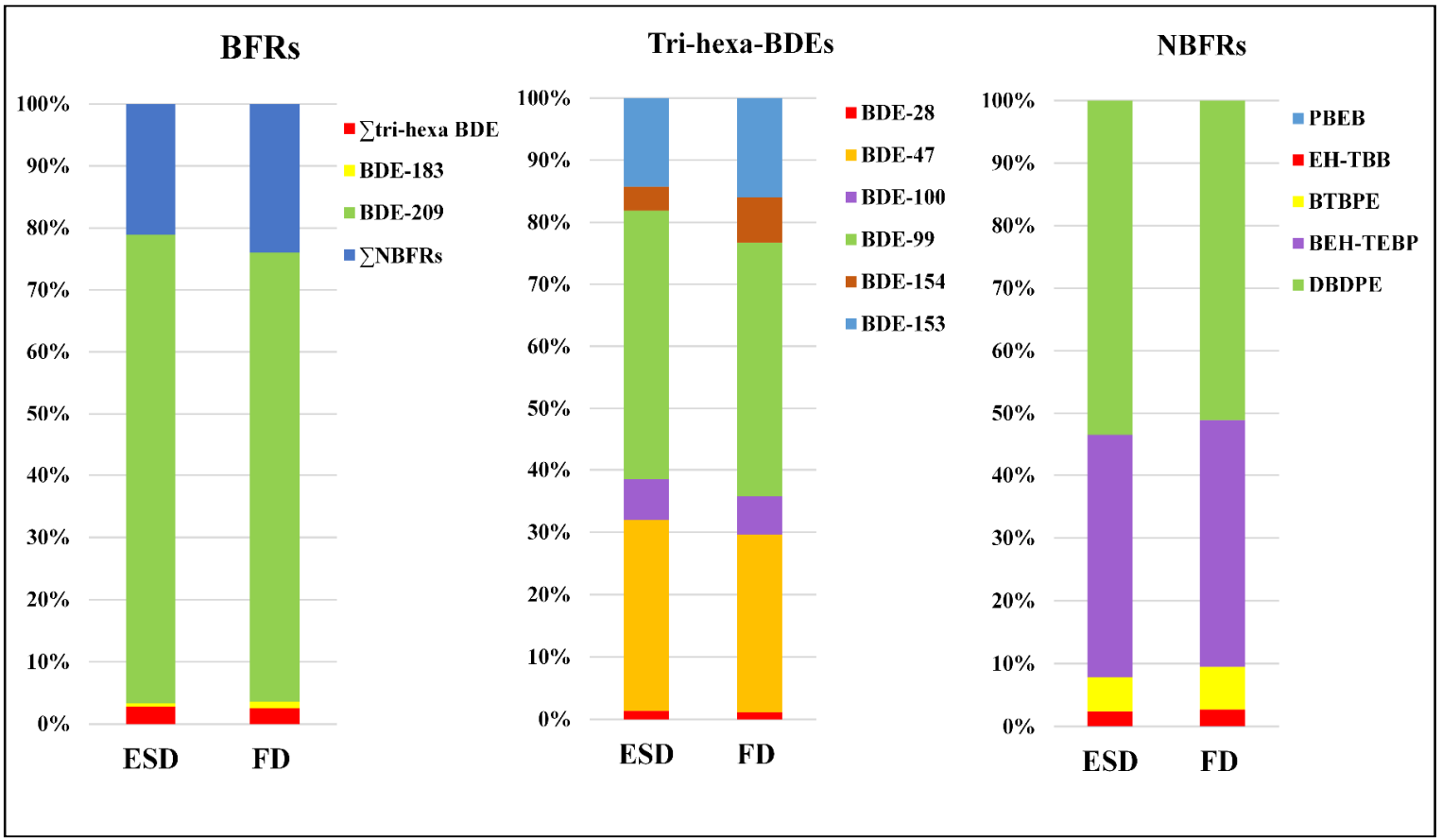
**Table 7.4: Detection frequency (%) of PBDEs and NBFRs in elevated surface dust (ESD) and floor dust (FD) samples**

| Analyte | ESD (n= 18) | FD (n=18) |
|---|---|---|
| BDE-28 | 61 | 44 |
| BDE-47 | 94 | 83 |
| BDE-100 | 67 | 50 |
| BDE-99 | 94 | 78 |
| BDE-154 | 67 | 61 |
| BDE-153 | 61 | 72 |
| BDE-183 | 94 | 94 |
| BDE-209 | 100 | 100 |
| PBEB | 72 | 44 |
| EH-TBB | 78 | 61 |
| BTBPE | 72 | 78 |
| BEH-TEBP | 100 | 89 |
| DBDPE | 100 | 100 |

The three main formulations (Penta-BDE, Octa-BDE and Deca-BDE) are represented in this study by $\Sigma_6$tri-hexa-BDEs as an indicator of Penta-BDE, BDE-183 as an indicator of Octa-BDE and BDE-209 as an indicator of Deca-BDE. $\Sigma_6$tri-hexa-BDEs refers to the summation

of six congeners, BDE-28, BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154. Among all the target BFRs, BDE-209 was predominant with average percentage contributions to ΣBFRs (sum of $\Sigma_6$tri-hexa-BDEs, BDE-209 and $\Sigma_5$NBFRs) of 75.6%, 72.4% in ESD and FD respectively. The next most abundant BFR group was $\Sigma_5$NBFRs (summation of five compounds PBEB, EH-TBB, BTBPE, BEH-TEBP, and DBDPE) which made average percentage contributions of 21% and 24% in ESD and FD respectively. $\Sigma_6$tri-hexa-BDEs and BDE-183 made the lowest average percentage contributions of our target BFRs, specifically 2.8% and 2.6% for $\Sigma_7$tri-hexa-BDEs and 0.5% and 1.1 for BDE-183 in ESD and FD respectively. Of our target NBFRs, DBDPE predominated with corresponding mean percentage contributions to $\Sigma_5$NBFRs of 53.6% and 51.1%, followed by BEH-TEBP with percentage contributions of 38.6% and 39.4% in ESD and FD respectively. Concentrations of EH-TBB, BTBPE and PBEB combined were only 7.9 % and 9.5 % $\Sigma_5$NBFRs in ESD and FD respectively. Of our target tri-hexa-BDEs, BDE-99 and BDE-47 made the highest average contributions to $\Sigma_7$tri-hexa-BDEs of 43.3% and 41.0% for BDE-99 and 30.7% and 28.5% for BDE-47, in elevated surface dust and floor dust respectively. The average percentage contributions of the rest of our target tri-hexa-BDEs (BDE-28, BDE-100, BDE-154 and BDE-153) to $\Sigma_6$tri-hexa-BDEs ranged from 1.1 % of BDE-28 in FD to 16 % of BDE-153 in ESD. Figure 7.1 illustrates distribution profiles of our target compounds as groups and as individual compounds in BFRs, NBFRs and tri-hexa-BDEs in both ESD and FD.

**Figure 7.1: Distribution profiles of PBDEs and NBFRs in the three main groups (BFRs = all the target compounds, tri-hexa-BDEs = BDE-28, BDE-47, BDE-100, BDE-99, BDE-154 and BDE-153, and NBFRs = the five target NBFRs) in elevated surface dust (ESD) and floor dust (FD)**



### 7.5.2 Concentrations of PBDEs and NBFRs in house dust samples from Iraq

The highest concentration of total PBDEs in indoor dust (3910 ng/g) was found in an ESD sample, with the lowest concentration (217 ng/g) found in an FD sample, with average concentrations of 1212 and 800 ng/g in ESD and FD respectively. $\Sigma_5$NBFR concentrations ranged between 89 ng/g in a floor dust sample to 742 ng/g in an ESD sample, with average concentrations of 324 and 252 ng/g in ESD and FD respectively. Average concentrations of BFRs with detection frequencies > 60% (PBDEs; BDE-47, -99, -153, -154, -183, and -209 and NBFRs; EH-TBB, BTBPE, BEH-TEBP, and DBDPE) in measured house dust samples from Iraq, with standard deviation (y error bar) in both elevated surface dust (ESD) and floor dust (FD), are illustrated in Figure 7.2. As mentioned earlier, BDE-209 was the predominant congener with maximum concentrations of 3850 ng/g in an ESD sample and 2760 ng/g in a FD sample, alongside average concentrations of 1160 ng/g and 762 ng/g in ESD and FD respectively. This is about 27 and 28 times higher than the average concentration of Penta-BDE congeners (represented by $\Sigma_6$tri-hexa-BDE) and 148 and 69 times higher than the average concentration of BDE-183 (an indicator of Octa-BDE) in ESD and FD respectively. This may reflect substantial past and ongoing use of Deca-BDE and the restrictions on Penta-BDE and Octa-BDE. The second most abundant compound was DBDPE with an average concentration of 173 ng/g and 129 ng/g followed by BEH-TEBP with an average concentration of 125 ng/g and 99.5 ng/g in ESD and FD respectively. Average concentrations of other individual contaminants ranged from 0.14 ng/g for PBEB in FD and 18.5 ng/g for BDE-99 in ESD. Table 7.5 presents summary statistics for PBDE congeners and NBFRs.

To the best of our knowledge PBDEs and NBFRs are not produced in Iraq, and we thus assume the sources of these chemicals are imported consumer products.

**Figure 7.2: Average concentrations of PBDEs and NBFRs in elevated surface dust (ESD) and floor dust (FD) with standard deviation (y error bar)**

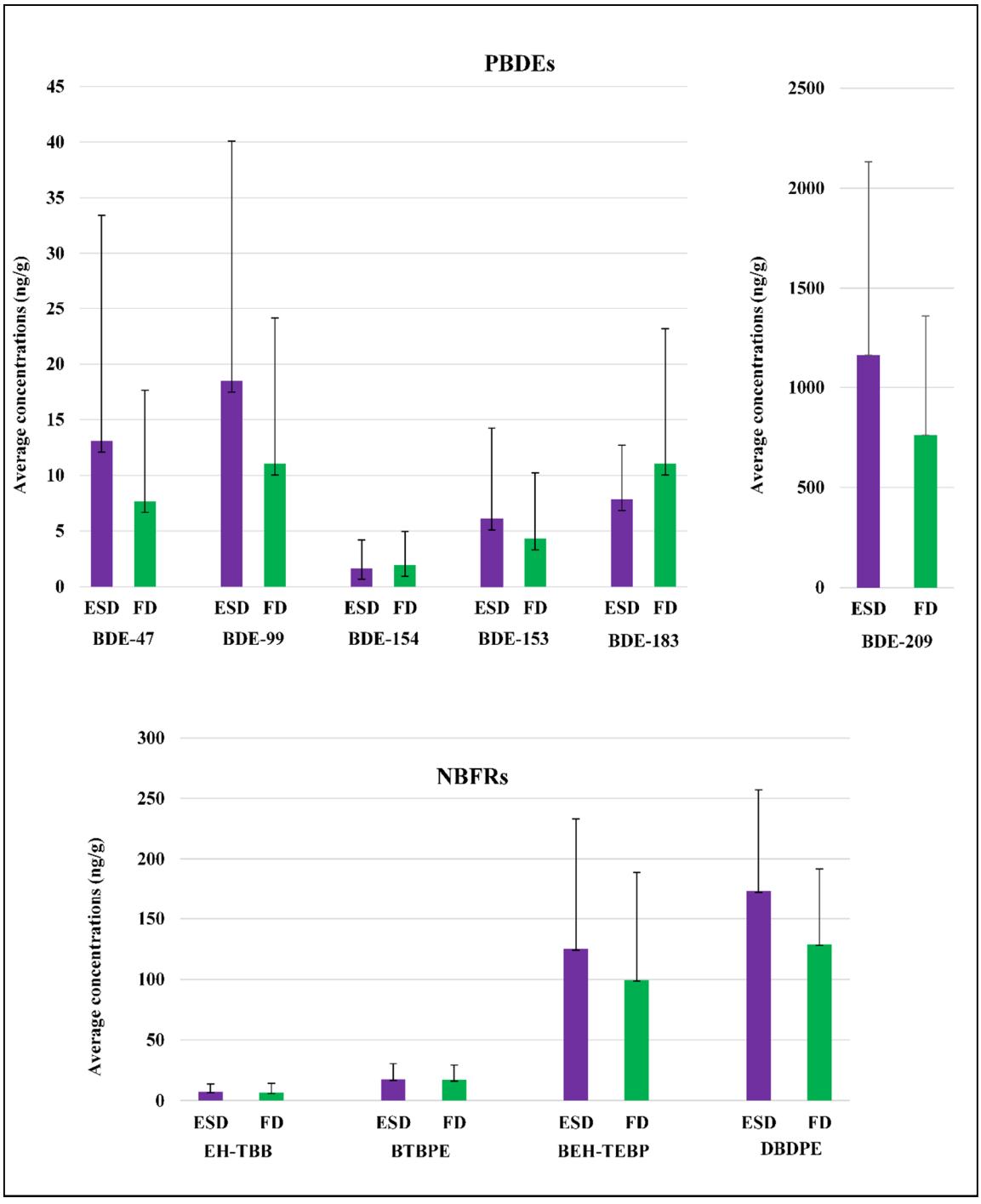


**Table 7.5: Concentrations of eight PBDE congeners (BDE-28, 47, 99, 100, 153, 154, 183, and 209) and five NBFRs (PBEB, EH-TBB, BTBPE, BEH-TEBP, and DBDPE) in samples of both ESD and FD from Iraqi homes**

| Compound | Sample Type | Mean | Minimum | Maximum | Median | 5th %ile | 95th %ile |
|---|---|---|---|---|---|---|---|
| BDE-28 | ESD | 0.57 | <0.1 | 1.82 | 0.43 | <0.1 | 1.55 |
| BDE-28 | FD | 0.31 | <0.1 | 1.2 | <0.1 | <0.1 | 1.11 |
| BDE-47 | ESD | 13.1 | <0.1 | 84.8 | 6.32 | 2.58 | 49.8 |
| BDE-47 | FD | 7.66 | <0.1 | 37.6 | 3.6 | <0.1 | 28.2 |
| BDE-99 | ESD | 18.5 | <0.1 | 73.8 | 13 | <0.2 | 71.7 |
| BDE-99 | FD | 11.0 | <0.1 | 49.2 | 6.67 | <0.2 | 36.1 |
| BDE-100 | ESD | 2.8 | <0.2 | 12.8 | 1.14 | <0.2 | 8.72 |
| BDE-100 | FD | 1.64 | <0.2 | 7.43 | 0.6 | <0.2 | 5.48 |
| BDE-153 | ESD | 6.09 | <0.01 | 25.1 | 0.73 | <0.01 | 20.7 |
| BDE-153 | FD | 4.32 | <0.01 | 16.9 | 0.54 | <0.01 | 14.3 |
| BDE-154 | ESD | 1.67 | <0.1 | 8.89 | 0.74 | <0.1 | 6.22 |
| BDE-154 | FD | 1.94 | <0.1 | 11.3 | 0.61 | <0.1 | 6.56 |
| BDE-183 | ESD | 7.85 | <0.2 | 18.6 | 6.9 | 0.88 | 15.2 |
| BDE-183 | FD | 11.1 | <0.2 | 46.5 | 7.5 | 1.88 | 37.6 |
| BDE-209 | ESD | 1160 | 277 | 3850 | 865 | 360 | 3270 |
| BDE-209 | FD | 762 | 193 | 2760 | 612 | 306 | 1590 |
| PBEB | ESD | 0.41 | <0.1 | 1.52 | 0.25 | <0.1 | 1.42 |
| PBEB | FD | 0.14 | <0.1 | 0.55 | <0.1 | <0.1 | 0.45 |
| EH-TBB | ESD | 7.49 | <1.3 | 20.6 | 6.15 | <1.3 | 19.9 |
| EH-TBB | FD | 6.8 | <1.3 | 28 | 5.28 | <1.3 | 16.6 |
| BTBPE | ESD | 17.5 | <9 | 43.7 | 15.2 | <9 | 43.1 |
| BTBPE | FD | 17.1 | <9 | 50.7 | 14.1 | <9 | 32.2 |
| BEH-TEBP | ESD | 125 | 33.9 | 412 | 82.7 | 47.8 | 368 |
| BEH-TEBP | FD | 99.5 | <6.8 | 294 | 64.2 | <6.8 | 248 |
| DBDPE | ESD | 173 | 58.1 | 351 | 183 | 64.9 | 295 |
| DBDPE | FD | 129 | 33 | 269 | 125 | 33 | 214 |
| ∑tri-hexa BDE[a] | ESD | 42.7 | 0.33 | 200 | 24.8 | 5.42 | 162 |
| ∑tri-hexa BDE[a] | FD | 26.9 | 1.31 | 108 | 15.8 | 2.3 | 91.4 |
| ∑PBDE[b] | ESD | 1210 | 294 | 3910 | 924 | 382 | 3300 |
| ∑PBDE[b] | FD | 800 | 217 | 2810 | 635 | 333 | 1610 |

[a]Sum of tri-hexa-BDE 28, 47, 99, 100, 153 and 154.

[b]Sum of PBDEs 28, 47, 99, 100, 153, 154, 183 and 209

### 7.5.3 Comparison with available literature data

To the best of our knowledge, there are no previous reports of concentrations of PBDEs and NBFRs in indoor dust in Iraq, and very limited reports of these contaminants in the Middle East (Gevao et al., 2006; Ali et al., 2013; Hassan and Shoeib, 2015). In floor dust samples, median concentrations of BDE-47, BDE-99, BDE-183 and BDE-209 in Basrah, Iraq exceeded generally those of Egypt, and Pakistan by factors of 2.1, 2.5, 6.8 and 40.2 for Egypt (Hassan and Shoeib, 2015) and 2.8, 3.9, 5.0 and 4.4 for Pakistan (Ali et al., 2013) respectively. In elevated surface dust samples, the levels of BDE-47, BDE-99, BDE-183 and BDE-209 exceeded those from Vietnam (Tue et al., 2013) by factors of 1.5, 3.6, 2.7 and 5.4 respectively. However, PBDEs in this study are at the lower end of those reported globally, and in keeping with previous studies are substantially lower than those reported for North America. Table 7.6 places our data for PBDEs in dust from Iraqi homes sampled in 2013 with those from selected related studies that have been published since 2008 from different countries in Asia, Africa, Europe, North America and Australia.

In terms of the congener pattern of PBDEs, the comparatively low abundance of BDE-47 and 99 observed in this study suggests limited use of the Penta-BDE formulation in Iraq. In contrast, the dominance of BDE-209 implies the extensive application of the Deca-BDE product. Of note is the comparatively elevated abundance of BDE-183, which suggests relatively high application of the Octa-BDE formulation in Iraq. No relationships between BFR concentrations in dust and room contents, ventilation type etc. were apparent.

For NBFRs, Table 7.7 places our data for Iraqi homes in context with the more limited international database available. As with the PBDEs, concentrations of our target NBFRs in this study are at the lower end of those reported previously, but lying more towards the mid-range, particularly for BTBPE and DBDPE. Moreover, in line with several previous studies, the ratio of EH-TBB: BEH-TEBP differs from the ratio observed in the commercial FM550 product (4:1) which suggests FM-550 is not the only source of these compounds.

**Table 7.6: Comparison of median concentrations (ng/g) of PBDEs detected in floor dust (FD) and elevated surface dust (ESD) in this study with previous reports.**

| Country | Sampling year | Sample Type | n | BDE-28 | BDE-47 | BDE-99 | BDE-100 | BDE-153 | BDE-154 | BDE-183 | BDE-209 | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Iraq | 2013 | FD | 18 | <0.1 | 3.6 | 6.67 | 0.6 | 0.54 | 0.61 | 7.5 | 612 | This study |
| Egypt | 2013 | FD | 17 | 0.34 | 1.7 | 2.7 | 0.37 | 6.62 | 0.38 | 1.1 | 40.2 | Hassan and Shoeib, 2015 |
| Kuwait | 2011 | FD | 15 | n.a | 9.5 | 12 | 2.3 | 2.4 | 1.3 | 1.9 | 310 | Ali et al., 2013 |
| Pakistan | 2011 | FD | 15 | n.a | 1.3 | 1.7 | 0.3 | 0.6 | 0.4 | 1.5 | 138 | Ali et al., 2013 |
| Hong Kong | n.a | FD | 23 | 37.6 | 102 | 75.4 | 84.9 | 10.9 | 8.36 | 77.7 | 975 | Kang et al., 2011 |
| China | 2010 | FD | 14 | 1.45 | 5.28 | 3.44 | 0.52 | 1.59 | 0.48 | 3.73 | 1610 | Zhu et al., 2013 |
| UK | 2006 | FD | 20 | 0.53 | 13 | 23 | 4.2 | 5.2 | 3.3 | 13 | 2800 | Harrad et al., 2008b |
| Germany | n.a | FD | 20 | 0.1 | 5.7 | 9.2 | 1.6 | 2.1 | 1.1 | 9.3 | 950 | Fromme et al., 2014 |
| Sweden | 2008 | FD | 19 | 0.19 | 15 | 13 | 2.7 | 2.2 | 1.5 | 1.5 | 280 | Björklund et al., 2012 |
| Norway | 2012 | FD | 48 | 0.68 | 126 | 171 | 33.1 | 26 | 12.7 | 3.22 | 326 | Cequier et al., 2014 |
| USA | 2006 | FD | 28 | 14 | 410 | 820 | 160 | 110 | 89 | 16 | 1300 | Harrad et al., 2008b |
| Canada | 2006 | FD | 10 | 4.1 | 140 | 330 | 65 | 43 | 39 | 9 | 560 | Harrad et al., 2008b |
| Canada | 2007-2008 | FD | 116 | 4.5 | 280 | 350 | 67 | 42 | 25 | 14 | 1300 | Shoeib et al., 2012 |
| New Zealand | 2006 | FD | 20 | 0.65 | 24 | 51 | 8.9 | 5.4 | 5.1 | n.a. | n.a | Harrad et al., 2008b |
| Australia | n.a | FD | 10 | n.a | 60 | 100 | 18 | 13 | 9 | 14 | 730 | Sjödin et al., 2008a |
| Iraq | 2013 | ESD | 18 | 0.43 | 6.32 | 13 | 1.14 | 0.73 | 0.74 | 6.9 | 865 | This study |
| Sweden | 2008 | ESD | 18 | 0.78 | 38 | 25 | 5.5 | 6 | 2.9 | 3 | 520 | Björklund et al., 2012 |
| Sweden | n.a. | ESD | 10 | 1.3 | 42 | 52 | n.a. | 6.6 | n.a. | 12 | 320 | Thuresson et al., 2012 |
| Vietnam | 2008 | ESD | 6 | n.a. | 4.1 | 3.6 | n.a. | 1.4 | n.a. | 2.6 | 160 | Tue et al., 2013 |

n.a. not available

**Table 7.7: Comparison of median concentrations (ng/g) of NBFRs studied in floor dust (FD) and elevated surface dust (ESD) in this study with previous reports**

| Country | Sampling year | Sample Type | n | PBEB | EH-TBB | BEH-TEBP | BTBPE | DBDPE | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Iraq (this study) | 2013 | FD | 18 | <0.1 | 5.3 | 64.2 | 14.1 | 125 | This study |
| Egypt | 2013 | FD | 17 | n.a. | 0.81 | 0.12 | 0.24 | n.a. | Hassan and Shoeib, 2015 |
| Pakistan | 2011 | FD | 31 | n.a. | 0.03 | 3.5 | 3.15 | 14 | Ali et al., 2012 |
| Belgium | 2008 | FD | 39 | n.a. | 1 | 13 | 2 | 153 | Ali et al., 2011a |
| Germany | n.a | FD | 20 | n.a. | <3.0 | 343 | <10 | 146 | Fromme et al., 2014 |
| Norway | 2012 | FD | 48 | <0.13 | 2.54 | 78.5 | 3.76 | 147 | Cequier et al., 2014 |
| USA | 2006 | FD | 19 | n.a. | 133 | 142 | 30 | 201 | Stapleton et al., 2008 |
| Canada | 2007-2008 | FD | 116 | n.a. | 120 | 99 | 30 | n.a | Shoeib et al., 2012 |
| Iraq (this study) | 2013 | ESD | 18 | 0.25 | 6.15 | 82.6 | 15.23 | 183 | This study |
| Vietnam | 2008 | ESD | 6 | n.a. | n.a. | n.a. | 7.1 | 40 | Tue et al., 2013 |
| China | 2008 | ESD+ FD | 27 | 0.15 | n.a. | n.a. | 6.47 | 2730 | Wang et al., 2010 |

n.a. not available

### 7.5.4 Comparison of BFR concentrations in floor and elevated surface dust

As seen in Figure 7.2, the differences in concentrations of the most PBDEs and NBFRs between elevated surface dust (ESD) and floor dust (FD) are obvious. Average concentrations of BDE-28, BDE-47, BDE-99, BDE-100, BDE-153 and BDE-209 in ESD were higher than FD by factors ranging between 1.4 -1.9, in contrast, on average, concentrations of BDE-183 in FD was higher than ESD by a factor of 1.4, while BDE-154 concentrations were almost comparable in both elevated surface dust and floor dust. For NBFRs, the average concentrations of BEH-TEBP and DBDPE in ESD exceeded those in FD by a factor of 1.3, while PBEB concentrations in ESD were 3 times higher than FD. No differences were observed between average concentrations of EH-TBB and BTBPE in ESD and FD.

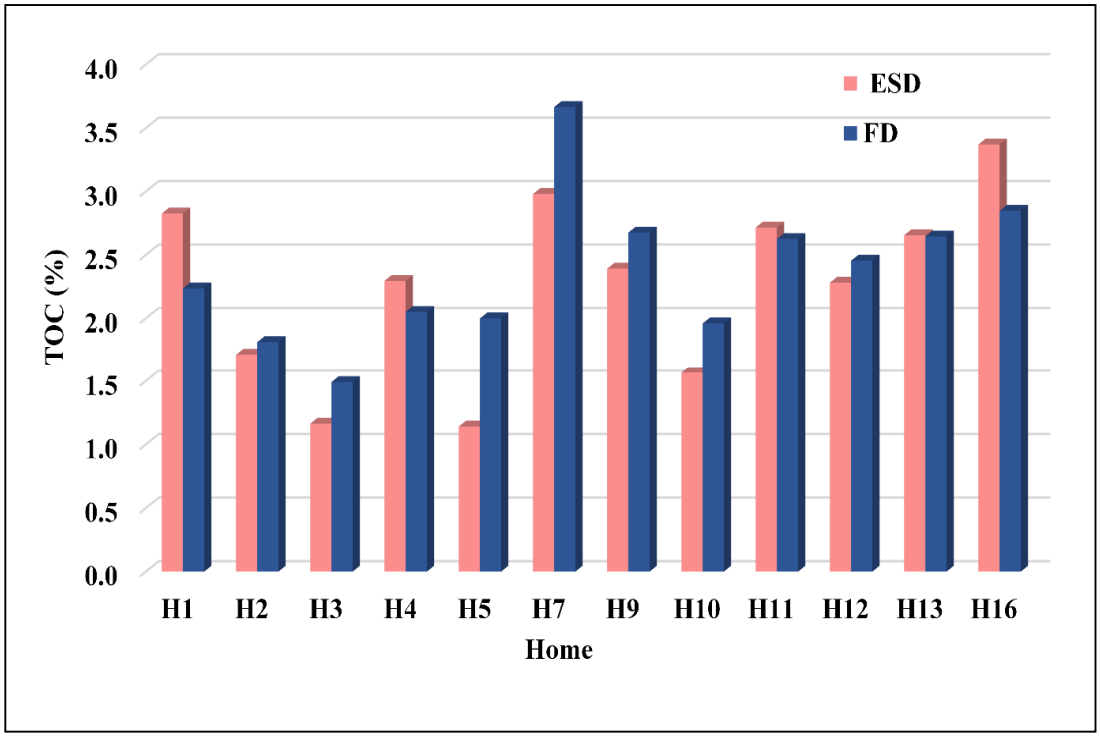
Following log transformation of concentrations expressed on a dry dust weight basis, a paired t-test was applied to test the hypothesis that concentrations of our target BFRs in ESD would exceed significantly those in FD. This revealed concentrations of BDE-28, BDE-99, BDE-209, PBEB, BEH-TEBP, and DBDPE in ESD to exceed significantly those in FD, with *P* values of 0.047, 0.014, 0.002, 0.003, 0.036, and 0.031 respectively. These findings were consistent with those of Björklund et al., (2012) who reported concentrations of PBDEs in elevated surface dust to exceed significantly those in vacuum cleaner dust, and with those of Cequier et al., (2014) who reported concentrations of BDE-209 and non-PBDEs in elevated surface dust to exceed (albeit not significantly) those in floor dust.

### 7.5.5 Organic carbon content of indoor dust from Iraq

To test the hypothesis that any differences in FR concentrations between ESD and FD were attributable to differences in organic carbon content of the dust, we measured the total organic content (TOC) as mentioned previously. Although paired t-test comparison of the TOC content of paired ESD and FD samples revealed no significant ($p > 0.05$) difference between the two dust categories, we tested the hypothesis that higher concentrations of TOC content in ESD lead to significantly higher concentrations of BFRs in such samples. To do so, we conducted a paired t-test comparison using log-transformed concentrations of BFRs normalised to the TOC content of both ESD and FD. Although based on a slightly smaller data set (n=12 homes for which the TOC content of paired ESD and FD samples were available), the results revealed concentrations of BDE-99, BDE-209, PBEB, BEH-TEBP, and DBDPE in ESD to exceed significantly those in FD, with *p* values of 0.028, 0.001, 0.015,

0.049, 0.003 respectively. This suggests that differences in organic carbon content between ESD and FD in our samples did not exert a substantial influence on the observed differences in BFR concentrations. In general, the organic carbon contents of Iraqi dust samples (1.1-3.66 %) were lower than UK dust samples (Chapter 5). Figure 7.3 compares the TOC contents of the elevated surface dust and floor dust samples analysed.

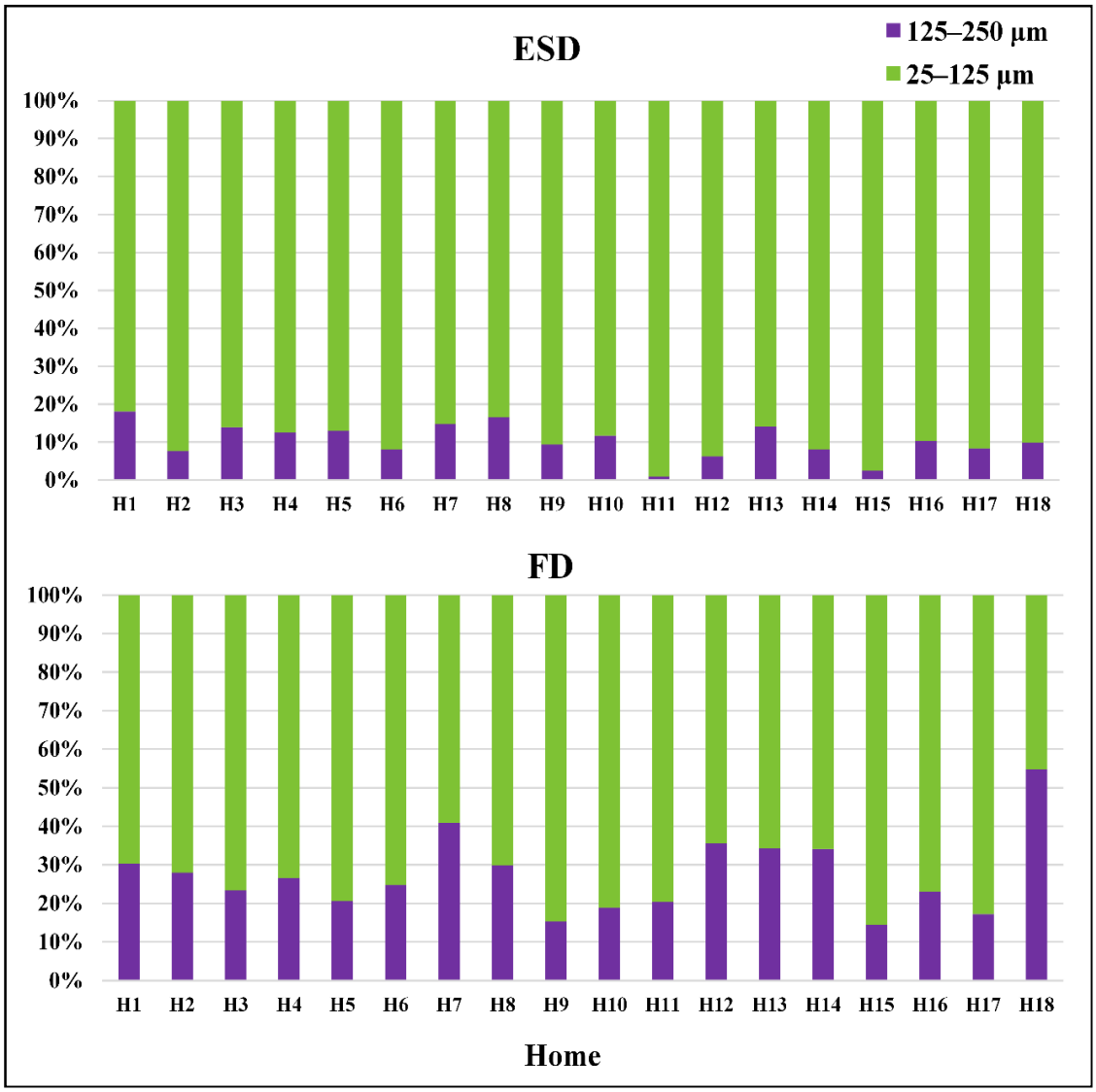
**Figure 7.3: Organic carbon contents (%) of elevated surface dust (ESD and floor dust (FD) from 12 homes**




### 7.5.6 Impact on BFR concentrations of dust particle size distribution

We next examined the hypothesis that differences in the particle size distribution found in ESD and FD in our study may explain the elevated concentrations of some BFRs in ESD. Prior to determination of BFR concentrations, we measured (via manual sieving and subsequent gravimetry) the mass of dust in each sample that fell into the following particle size distributions: < 125 µm and 125-250 µm. Results showed significantly ($p < 0.05$) higher proportions of particles < 125 µm in samples of ESD and of particles between 125 µm and 250 µm in FD. The average mass of dust fractions < 125 µm and 125-250 µm in the bulk dust were about 90% and 10% in ESD and 73% and 27% in FD respectively. Figure 7.4 shows the pattern of mass ratios between elevated surface dust and floor dust.

**Figure 7.4: Comparison of particle size distribution ratios in elevated surface dust (ESD) and floor dust (FD) in homes from Iraq**




While we combined these size fractions into a single sample for determination of BFRs, 86% of $\Sigma_7$tri-hepta-BDEs and BEH-TEBP, 77% of BDE-209 and 79% of DBDPE were associated with particle size < 125 µm in UK dust samples (Chapter 5, section 5.3.4). In addition, over 80% of ΣBDEs determined in a small number of US indoor dust samples have been reported to be present in particles <150 µm (Wei et al., 2009). We suggest that this is one plausible reason for the higher concentrations of some BFRs in ESD in our study (Chapter 5). Moreover, recent studies have pointed that BFR concentrations in fine dust particles are higher than in the largest particles (Cao et al., 2014a; 2014b; 2015; Kefeni et al., 2014; Chao et al., 2014).

An additional explanation for the high concentrations of BFRs in ESD compared to FD is because our elevated surface dust samples likely included dust that had been in direct contact with putative sources such as electronics and soft furnishings. Previous studies have shown that both direct source dust contact and abrasion are highly effective pathways via which BFRs may transfer from products to dust (Rauert et al., 2014a; Rauert and Harrad, 2015) and thus ESD sampled from such product surfaces will likely contain elevated concentrations of BFRs.

### 7.5.7 Relationship between concentrations of different BFRs

Significant positive linear correlation between concentrations of different contaminants in paired samples of FD and ESD indicates that similar factors likely influence the observed concentrations. One such factor may be common sources. We therefore evaluated our data for the existence of such correlations.

To do so, we subjected log-transformed concentrations of each of our target BFRs in ESD with those in the corresponding FD samples to Pearson correlation analysis. These analyses revealed that concentrations of several of our target PBDEs and NBFRs in FD samples were significantly correlated with those in ESD samples. Significant correlation ($p < 0.05$) was found for: BDE-47, BDE-99, BDE-154, BDE-209, BEH-TEBP, EH-TBB, and DBDPE, with respective correlation coefficient values of 0.855, 0.838, 0.780, 0.793, 0.803, 0.656, and 0.652. Note that correlation analyses were conducted only for those samples from homes in which the target BFR was detected in both ESD and FD. Similar results were obtained when we examined our data for correlations between organic-normalised concentrations of BFRs in the 12 sample pairs for which such data were available. This suggests that the sources of these contaminants in ESD and FD are similar.

### 7.5.8 Human exposure to BFRs via dust ingestion

We used our data on concentrations of BFRs in indoor dust to generate preliminary estimates of human exposure to our target contaminants via ingestion of dust. To evaluate the likely range of exposure we examined three scenarios for ESD and FD separately. The three scenarios are low-end, “typical” and high-end exposure, with the assumptions on which these are based are described in Chapter 1, section 1.11. As mentioned in Chapter 1, we assumed 100% absorption of intake and body weights of 70 kg and 12 kg for adults and toddlers

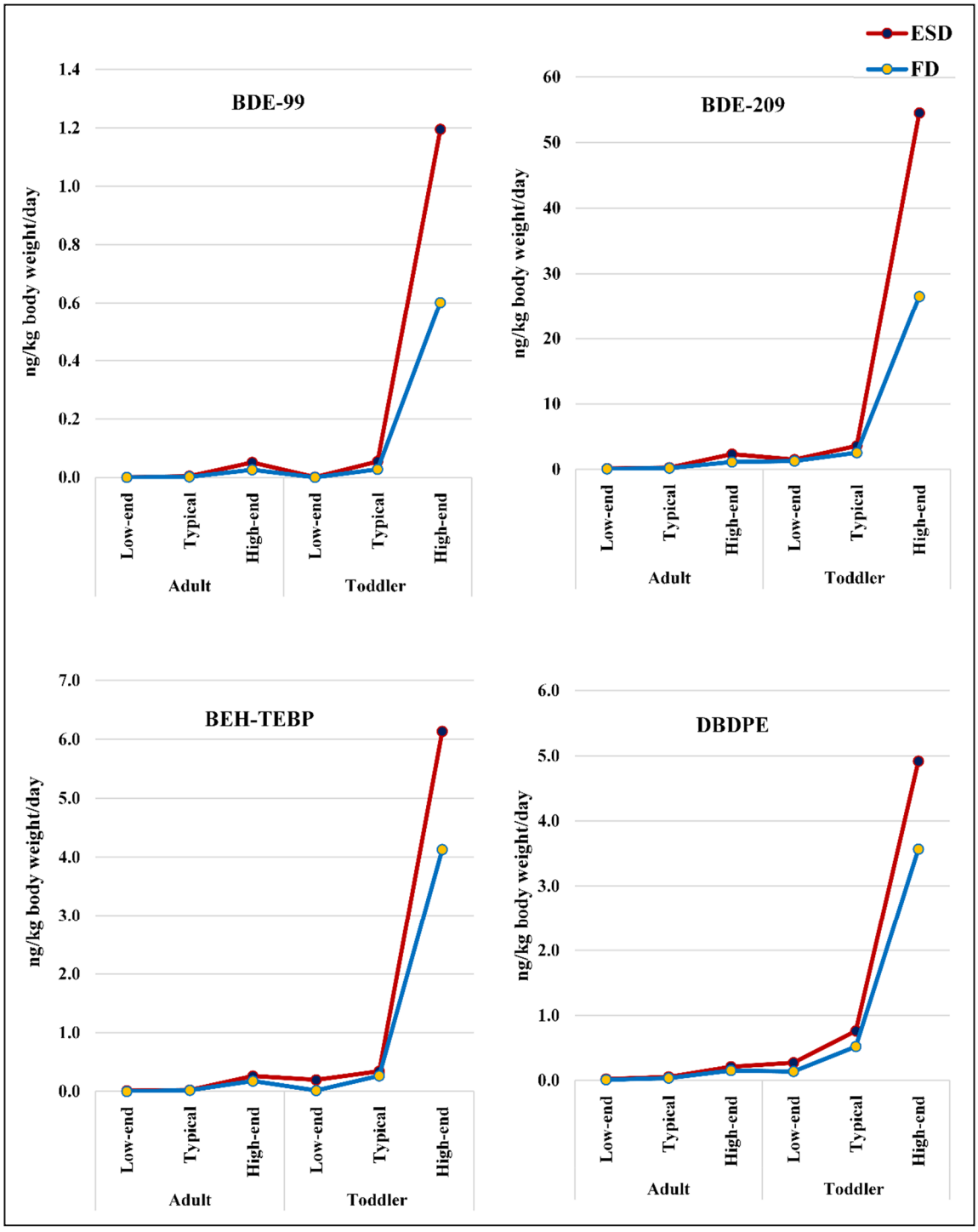
respectively. The resultant exposure estimates in ng/kg body weight/day for BDE-47, BDE-99, BDE-183, BDE-209, $\Sigma_6$tri-hexaBDE, ΣPBDE, EH-TBB, BTBPE, BEH-TEBP, and DBDPE are provided in Table 7.8. Our exposure estimates for both adults and toddlers for the Iraqi population are several orders below the corresponding RfDs (Chapter 1, Table 1.13)

**Table 7.8: Estimated exposure (ng/kg body weight/day) of adults and toddlers of PBDEs and NBFRs via dust ingestion in Basrah, Iraq**

| Compound | Dust | Adult | | | Toddler | | |
|---|---|---|---|---|---|---|---|
| | | Exposure Scenario | | | Exposure Scenario | | |
| | | Low-end | "Typical" | High-end | Low-end | "Typical" | High-end |
| BDE47 | ESD | <0.01 | <0.01 | 0.04 | 0.01 | 0.03 | 0.83 |
| BDE47 | FD | <0.01 | <0.01 | 0.02 | <0.01 | 0.01 | 0.47 |
| BDE99 | ESD | <0.01 | <0.01 | 0.05 | <0.01 | 0.05 | 1.19 |
| BDE99 | FD | <0.01 | <0.01 | 0.03 | <0.01 | 0.03 | 0.60 |
| BDE183 | ESD | <0.01 | <0.01 | 0.01 | <0.01 | 0.03 | 0.25 |
| BDE183 | FD | <0.01 | <0.01 | 0.03 | 0.01 | 0.03 | 0.63 |
| BDE209 | ESD | 0.10 | 0.25 | 2.33 | 1.50 | 3.60 | 54.48 |
| BDE209 | FD | 0.09 | 0.17 | 1.14 | 1.27 | 2.55 | 26.54 |
| Σtri-hexa BDE | ESD | <0.01 | 0.01 | 0.12 | 0.02 | 0.10 | 2.70 |
| Σtri-hexa BDE | FD | <0.01 | <0.01 | 0.07 | 0.01 | 0.07 | 1.52 |
| ΣPBDEs | ESD | 0.11 | 0.26 | 2.35 | 1.59 | 3.85 | 54.93 |
| ΣPBDEs | FD | 0.10 | 0.18 | 1.15 | 1.39 | 2.65 | 26.85 |
| EH-TBB | ESD | <0.01 | <0.01 | 0.01 | <0.01 | 0.03 | 0.33 |
| EH-TBB | FD | <0.01 | <0.01 | 0.01 | <0.01 | 0.02 | 0.28 |
| BTBPE | ESD | <0.01 | <0.01 | 0.03 | 0.02 | 0.06 | 0.72 |
| BTBPE | FD | <0.01 | <0.01 | 0.02 | 0.02 | 0.06 | 0.54 |
| BEH-TEBP | ESD | 0.01 | 0.02 | 0.26 | 0.20 | 0.34 | 6.14 |
| BEH-TEBP | FD | <0.01 | 0.02 | 0.18 | 0.01 | 0.27 | 4.13 |
| DBDPE | ESD | 0.02 | 0.05 | 0.21 | 0.27 | 0.76 | 4.92 |
| DBDPE | FD | 0.01 | 0.04 | 0.15 | 0.14 | 0.52 | 3.57 |
| $\Sigma_5$NBFRs | ESD | 0.04 | 0.08 | 0.48 | 0.53 | 1.18 | 11.24 |
| $\Sigma_5$NBFRs | FD | 0.03 | 0.07 | 0.33 | 0.39 | 0.98 | 7.74 |

Estimated exposure to BDE-99, BDE-209, BEH-TEBP and DBDPE via ingestion of: (a) elevated surface dust (ESD) and (b) floor dust (FD) is compared in Figure 7.5.

**Figure 7.5: Comparison of human exposure to BDE-99, BDE-209, BEH-TEBP and DBDPE via ingestion of: (a) elevated surface dust (ESD) and (b) floor dust (FD)**



According to Figure 7.5, the ratio of exposure estimates obtained assuming ingestion of: (a) ESD only, and (b) FD only were 2.0, 2.1, 1.5 and 1.4 for BDE-99, BDE-209, BEH-TEBP and DBDPE respectively. While this may suggest that previous exposure estimates based on ingestion of floor dust alone may underestimate exposure, it is plausible that this applies only to adults, who we hypothesise are more likely to ingest elevated surface dust than floor dust. In contrast, it is reasonable to suggest that crawling toddlers will ingest mainly floor dust, and as such, we believe that the elevated concentrations detected in elevated surface dust will exert little impact on toddler exposure.

## 7.6 Conclusions

This study reveals concentrations of several of our target BFRs to be significantly higher in dust collected from elevated surfaces like chairs and tables than in floor dust from the same rooms. This suggests that previous studies that base estimates of adult exposure via dust ingestion on floor dust, may underestimate exposure. Such underestimation is less likely for toddlers as observation suggests they are far more likely to ingest floor dust. Concentrations of PBDEs and NBFRs in dust from both elevated surfaces and floors in Basrah, Iraq were at the lower end of contamination levels reported elsewhere in the world. In line with other studies from outside North America, the PBDE contamination pattern suggests that use in Iraq of the Deca-BDE formulation, exceeds substantially that of Penta-BDE. Our data also suggest that the use of the Octa-BDE formulation has been higher in Iraq than in some other regions. Our data represent a valuable baseline against which responses to actions designed to limit exposure to PBDEs may be evaluated in the future. Our estimates of exposure to our target BFRs via dust ingestion for the Iraqi population fall well below the relevant health-based limit values.

# CHAPTER 8

## SUMMARY AND CONCLUSIONS

Polybrominated diphenyl ethers (PBDEs) and "novel" brominated flame retardants (NBFRs) are chemicals added to a wide range of consumer products (electrical and electronic equipment, textiles, polyurethane and polystyrene foams) to meet flame retardancy standards set by various jurisdictions worldwide (Danish EPA, 2013; USEPA, 2014). Since in most applications these chemicals are used additively, they can transfer from such products into the environment. Evidence of their persistence and capacity for bioaccumulation, coupled with concerns about their adverse health effects have led to widespread bans and restrictions on the manufacture and use of PBDEs and their listing under the Stockholm Convention on Persistent Organic Pollutants (POPs) (UNEP, 2008; 2013a; 2013b), which has resulted in increased production and use of new brominated flame retardants (NBFRs e.g. EH-TBB, BEH-TEBP, BTBPE and DBDPE) as PBDE replacements. The similarity in physicochemical properties and applications between PBDEs and NBFRs leads to the hypothesis that human exposure to NBFRs will occur via similar pathways (Covaci et al., 2011).

Of the main exposure routes (air inhalation, food intake and ingestion or dermal absorption of indoor dust), a number of studies have revealed a significant positive correlation between the concentrations of BFRs in indoor dust and human tissues such as human milk (Thomsen et al., 2009), hair (Kang et al., 2011) and serum samples (Stapleton et al., 2012); suggesting that indoor dust ingestion is a major pathway of exposure to such chemicals. Hence, any human exposure assessment must include a strong focus on indoor dust ingestion, particularly for young children, as hand-to-mouth behaviour may be significant for this age group (Harrad et al., 2010a). Because dust ingestion is likely related to hand-to-mouth behaviour, dust loading and particle size that may affect adherence of dust to the skin are of importance. In addition, because indoor consumer products constitute potential BFR emission sources, BFR contamination of indoor dust and thus exposure will vary in both time and space depending on variations in the proximity of dust sampling locations to putative sources.

Given the above, the main aim of this project was to investigate factors affecting BFR concentrations in indoor dust. Specifically these are: variability across locations and over time, dust properties and sampling method. In addition, we aim to determine the extent to

which such factors affect human exposure assessments. The main achievements and outcomes of this thesis are summarised below.

## 8.1 Spatial variability in concentrations of BFRs in indoor dust

In this strand, the following hypothesis was addressed: *human exposure assessments of PBDEs and NBFRs via dust ingestion are affected by within-room and within-home spatial variability*. To test this hypothesis, dust samples were collected from nine rooms within three homes in Birmingham, UK. From each room, one sample was collected from elevated surfaces and two samples from two different floor areas. Variability in concentrations of PBDEs and NBFRs was evaluated using a t-test and a repeated measures ANOVA test applied to samples taken from: a) two different floor areas, b) elevated surface and floor dust, and c) different rooms in the same home. In dust samples taken from different floor areas within the same room, no significant difference in BDE-209 concentrations was observed, while $\Sigma_7$tri-hepta-BDEs (in three rooms), BEH-TEBP (in one room) DBDPE (in two rooms) and $\Sigma_5$NBFRs (in two rooms) were significantly ($p$ = < 0.05) different between different floor areas in the same room. Such spatial variability in BFR concentrations is likely driven by variable distances from potential emission sources, which is influenced by room dimensions. These outcomes indicate that dust from a single area within a given room will likely not provide a representative measure of contamination in the room overall. Hence, the number of floor dust samples collected should be increased as room dimensions increase. In dust samples from different surfaces (elevated surfaces and floor), with the exception of DBDPE, BFR ($\Sigma_7$tri-hepta-BDEs, BDE-209, BEH-TEPB and DBDPE in 7, 4, 5 and 4 of 9 rooms respectively) concentrations in dust samples from elevated surfaces exceeded significantly ($p < 0.05$) those from the floor in the same room. These results indicate that both floor and elevated surface dust should be considered for human exposure assessment, particularly for adults who likely are in contact with elevated surfaces more than the floor. Among the nine rooms investigated, the limited within-home variability between different rooms observed is likely attributable to differences in the putative sources present in the rooms studied. Due to the substantial within-room and within-home spatial variability observed, exposure estimates based on one specific floor area, floor surface only or one room may not be an entirely representative metric of exposure.

## 8.2 Temporal and seasonal variability in concentrations of BFRs in indoor dust.

This strand of work addressed the following hypothesis: *temporal and seasonal variability in PBDE and NBFR concentrations in indoor dust could influence human exposure assessments via dust ingestion*. To test this hypothesis, concentrations of PBDEs and NBFRs were monitored (month-to-month) for nine months covering both colder and warmer seasons in different locations and different surfaces within the same room in nine rooms within three homes. The relative standard deviation of concentrations of individual BFRs in 18 floor area samples ranged between 4% and 159% and in 9 elevated surface dust samples ranged between 9% and 117%. In both instances, these RSD values exceeded those obtained from replicate analysis of SRM2585, which ranged from 9% to 14%. This observed temporal variation in BFR concentrations is likely attributable to concomitant changes in room contents with respect to putative sources of target BFRs. $\Sigma_7$tri-hepta-BDEs concentrations were associated with the presence/absence of electronic devices and old foam furniture, while those in BDE-209 were associated with carpets and fabric materials. BEH-TEBP variability was associated with new bedroom furnishings, while DBDPE temporal variability was not associated with any specific source. However, changes in room contents did not explain the gradual decline in concentrations of BEH-TEBP in the bedrooms of one home over the first seven months of sampling. This might instead reflect gradual attainment of equilibrium between the gas phase and particulate phase of this BFR in indoor air. In addition to high RSD values, maximum: minimum ratios for BFR concentrations in the same room and floor area over the sampling period ranged from 1.1 to 71.4.

Noticeable seasonal variability in BFR concentrations were also observed between colder and warmer seasons, in 13 out of 17 floor areas, average concentrations of $\Sigma_8$tri-deca-BDEs were higher in colder seasons than warmer, while in the same number of floor locations, $\Sigma_5$NBFRs were higher in warmer seasons, with the exception of DBDPE. In general, average concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209 and BEH-TEBP in elevated surface dust samples were higher in warmer seasons than in colder, while in floor dust, average concentrations of BDE-209 were comparable in both colder and warmer seasons. With the exception of $\Sigma_8$tri-deca-BDEs in two floor areas and $\Sigma_5$NBFRs in four floor areas, no significant differences in concentrations of these two groups were apparent between warmer and colder seasons. Higher concentrations in colder seasons were only observed for BDE-209

and DBDPE, which might be due to the low vapour pressure of these compounds which facilitate partitioning to indoor dust.

To assess the extent to which temporal and seasonal variability may affect human exposure assessment, we compared the RSD values for selected BFRs and examined the extremes of exposure assessment using maximum: minimum concentration ratios for a given room. Our findings revealed uncertainty of exposure assessments for BFRs based on a single dust sample taken from a given area at a given point in time.

## 8.3 Selection of particle size fraction is an important factor for exposure assessments

In this strand of activity we addressed the following hypothesis: *BFR concentrations will increase with decreasing particle size fraction, which will substantially affect exposure assessments.* To test this hypothesis, BFRs were analysed in five paired samples of floor dust and elevated surface dust (i.e. elevated surface and floor dust collected from the same rooms) after fractionating into three different particle size fractions, large (125-250 µm), medium (63-125 µm), and fine (25-63 µm). A repeated measures ANOVA test revealed that while concentrations of lower brominated compounds (tri-hepta-BDEs and BEH-TEBP) are significantly higher in the fine fraction; concentrations of BDE-209, BTBPE, EH-TBB, and DBDPE are not significantly different between different dust particle size fractions. As no significant differences were observed between the organic carbon content of dust from different particle size fractions, we believe such variations in concentrations of lower brominated compounds (higher vapour pressure) are more likely due to the greater surface area to volume ratios of finer particles. While this is likely the dominant influence for more volatile BFRs, for which atmospheric deposition is the main pathway via which BFRs transfer from sources to indoor dust; we suggest it is less important for less volatile BFRs, for which abrasion of sources and transfer via direct source: dust contact are more important source-to-dust transfer pathways. Due to the substantial differences we observed in BFR concentrations between different particle size fractions, we suggest that for human exposure assessment, particle size selection is an important consideration. Our findings indicate that analysing finer particles (25-63 µm) yields higher exposure estimates than if a larger size fraction (25-250 µm) is analysed. It is difficult to compare concentrations of dust samples with different particle size fractions.

## 8.4 Sampling both elevated surfaces dust and floor dust to reflect adult and toddler exposure assessments.

This strand of work addressed the following hypothesis: *concentrations of PBDEs and NBFRs in dust from elevated surfaces will exceed significantly those in floor dust from the same microenvironment*. To test this hypothesis, elevated surface dust (present on surfaces like tables, shelves and chairs) and floor dust were collected at the same time from 18 homes in Basrah, Iraq. A t-test was applied to investigate any differences in BFR concentrations from the two dust categories. Our findings revealed that BDE-28, BDE-99, BDE-209, PBEB, BEH-TEBP and DBDPE concentrations in elevated surface dust exceeded significantly ($p < 0.05$) those in floor dust from the same living room with $p$ values of 0.047, 0.014, 0.002, 0.003, 0.036, and 0.031, respectively. As no significant differences were observed between the organic carbon content of elevated surface and floor dust, we examined the particle size distribution of the two dust categories. The mass of coarse (125-250 μm) and fine (< 125 μm) particles was measured in both elevated surface dust and floor dust. The findings showed that finer particles were significantly ($p < 0.05$) more abundant in elevated surface dust, while coarse particles were significantly more prevalent in floor dust. This suggests that the greater relative abundance of finer particles in elevated surface dust may account for the elevated concentrations of BFRs in such dust compared to floor dust.

Our findings for UK dust samples testing the hypotheses outlined in sections 8.1 and 8.3 were enhanced by the results obtained from these Iraqi dust samples. T-test analysis revealed that with the exception of DBDPE, concentrations of BFRs in UK elevated surface dust exceeded significantly those in floor dust.

Due to such differences between BFR concentrations in elevated surface dust and floor dust, it is likely that previous studies estimating adult exposure via ingestion of floor dust only, may underestimate exposure. This underestimation is less likely for toddlers who are more likely to ingest floor dust.

## 8.5 Organic carbon content cannot explain the higher concentrations of BFR in finer particle size fractions and elevated surface dust.

In this strand of research, we tested the following hypothesis: *differences in BFR concentrations between elevated surfaces and floor dust or between different particle size fractions could be attributed to particle size differences in the total organic carbon (TOC) content*. We tested this hypothesis in an effort to explain our findings in sections 8.3 and 8.4. TOC was measured in Iraqi dust samples (from elevated surface dust and floor dust) and UK dust samples (also from elevated surfaces and floor dust, but fractionated into three different particle size fractions). Although comparison of TOC via repeated measures ANOVA test (for different particle size fraction dust samples) and t-test (for paired elevated surface and floor dust samples) revealed no significant ($p > 0.05$) differences between TOC in different particle size fractions nor between elevated surface and floor dust, we tested the hypothesis that higher concentrations of TOC content in fine particles or in elevated surface dust lead to significantly higher concentrations of BFRs in such samples. Our findings in both UK and Iraqi dust samples revealed that that the organic carbon of dust cannot explain the higher concentrations of some BFRs in the finest particle size fractions nor in elevated surface dust samples.

On the other hand, despite the differences in geography, climate and lifestyle between the UK and Iraq, higher organic carbon contents in UK dust samples (15.5 - 48.0%) compared with Iraqi dust samples (1.1- 3.7 %) could contribute to the higher concentrations of BFRs in the UK compared with Iraq.

## 8.6 Dust sampling approach affects BFR concentrations and consequent human exposure assessments

This strand of work aimed to address the following hypothesis: *BFR concentrations in researcher-collected dust (RCD) will differ significantly from those in household vacuum dust (HHVD) samples*. To examine this hypothesis, 2 floor dust samples were collected by the researcher from the living room (RCDL) and bedroom (RCDB) from 12 homes in the UK, with an additional third sample taken from the contents of a vacuum cleaner bag donated by the householder. One way repeated measures ANOVA tests were applied. Our findings revealed that BFR concentrations in RCD were higher than those in HHVD, and significantly higher for BDE-99, BDE-153, $\Sigma_6$tri-hexa-BDEs and – to some extent - BEH-TEBP. This

might be due to volatilisation of lower brominated BFRs as a result of the long residence times of dust in the household vacuum. In addition, small particles may have been lost during collection and transfer processes from the vacuum bag. As mentioned in section 8.3, concentrations of lower brominated BFRs and BEH-TEBP are significantly higher in the finest particles, thus lower concentrations of lower brominated BFRs and BEH-TEBP in HHVD could be attributed to loss of the finest particles. Due to these outcomes, we found that high-end exposure assessments using HHVD will be underestimated for lower brominated compounds and BEH-TEBP by factors of 3.5, 2.7 and 1.3 for BDE-99, $\Sigma_6$tri-hexa-BDEs and BEH-TEBP respectively. However, HHVD could be a viable alternative to RCD for higher brominated BFRs such as BDE-209.

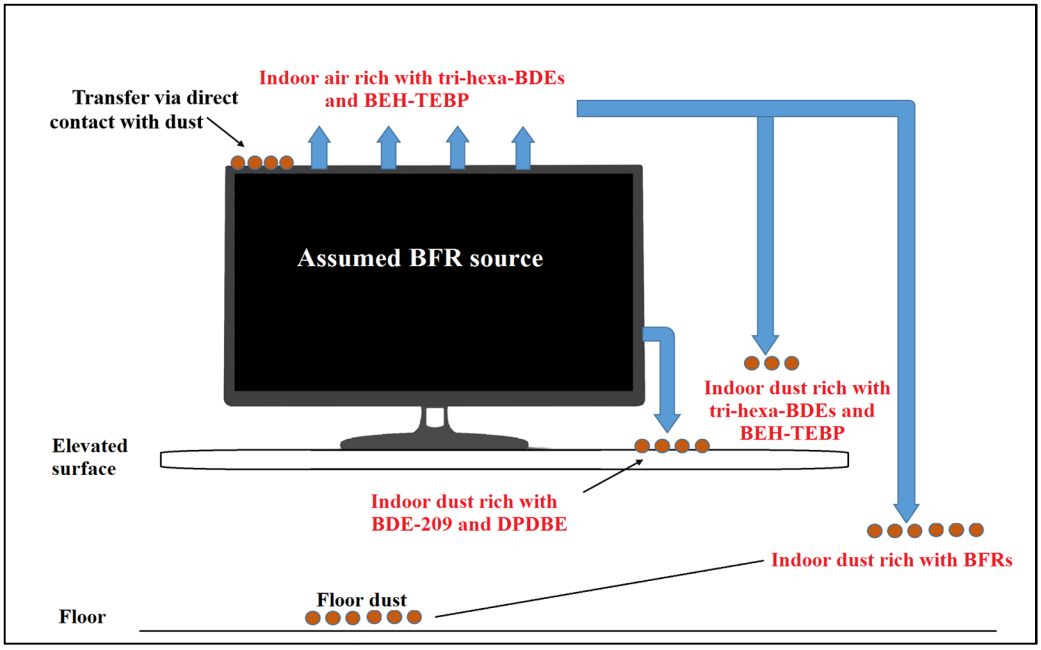
## 8.7 Dust loading of indoor settled dust may affect BFR concentrations.

This final strand of research addressed the following hypothesis*: under certain conditions, as a consequence of a "BFR dilution effect", a significant negative correlation between the logarithms of BFR concentrations and dust loadings is expected*. To test this hypothesis, we investigated the relationship between concentrations of BFRs (displaying detection frequencies > 90%) and dust loading ($g/m^2$) for 9 months in 17 separate floor areas within 9 rooms of three homes in the UK. This revealed that, in three out of seventeen individual floor areas, concentrations of lower brominated compounds (i.e. BDE-99 and $\Sigma_6$tri-hepta-BDEs) and BEH-TEBP decreased as dust loading increased, with a plot of Log (dust loading) versus Log BFR concentration showing a significant linear correlation with a negative slope. This implies that "dilution" has occurred in these rooms due to the high dust loading and indicates that the source of these compounds and of indoor dust are independent. However, in one sampled area, a positive correlation between DBDPE concentration and dust loading revealed that the sources of both dust and DBDPE are dependent, which suggested that DBDPE released to the indoor dust via abrasion of fibres or particles from treated material.

## 8.8 Potential pathways of PBDEs and NBFRs migrations into indoor dust

According to the experimental results, the three pathways of BFR migration into indoor dust are summarised in Figure 8.

**Figure 8.1: Pathways of PBDE and NBFR migration from potential source to indoor dust (adapted from Rauert et al (2014a)**




## 8.9 Research gaps and recommendations for future work

The body of the knowledge presented in this thesis makes a valuable contribution to understanding the main factors affecting assessments of human exposure via dust ingestion. However, significant research gaps still exist. To address these gaps, research is required to:

- Provide more data on spatial and temporal variability in concentrations of BFRs in indoor air at the same time as monitoring indoor dust. This will help understand BFR partitioning between the gas and particulate phases, which in turn may help explain the higher concentrations of lower brominated compounds in elevated surface dust and the finest particle size fractions.

- Monitoring indoor air, possibly via 'personal' air samplers to evaluate the significance of inhalation exposure versus dust ingestion for BFRs.

- Elucidate the mechanisms of transfer of BFR from treated products to indoor dust, particularly via direct source dust contact, as such understanding may help explain high concentrations of less volatile BFRs such as BDE-209 and BEH-TEBP in elevated surface dust.

- Provide more information to understand spatial and temporal variability in concentrations of BFRs from different microenvironment categories such as offices, workplaces, schools and nurseries. For human exposure assessment, we recommend sampling more than one floor dust sample depending on the dimensions of the microenvironments and all elevated surfaces at a height of 0.5-1.5 m. In addition, dust sampling should be conducted for 1 year, at least 1 time each season.

- Based on our findings and consistent with a recent report (USEPA, 2016) on human exposure assessment, we recommend analysis of a specific particle size range (< 150 µm), as these are most likely to adhere to hands.

- Elucidate the distribution pattern of BFR concentrations in different particle size fractions in indoor dust obtained via the two most-widely used sampling methods (researcher-collected and household vacuum) to test the hypothesis that a greater proportion of fine particles in researcher-collected dust account for the higher BFR concentrations observed in such dust compared to household vacuum cleaner dust.

- Understand debromination of BDE 209 to lower brominated congeners via natural sunlight, this may provide a possible explanation for higher concentrations of BDE-183 in dust samples in sunny and hot countries.

- Determine BFR body burdens alongside collection of indoor dust to understand which dust sampling approach (researcher-collected or household vacuum) yields the most biologically relevant dust measurement.

- Improve understanding of the physicochemical properties of NBFRs by conducting empirical studies. This is particularly important for BEH-TEBP TEBP given its similar behaviour to lower brominated PBDEs.

- Evaluate the wipe sampling method to collect dust from elevated surfaces, due to the insufficient quantity obtained via vacuuming elevated surfaces.

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**Appendix 2: *p* values obtained from the T-test comparison of concentrations of BFRs between the two floor areas (F1 and F2) within the same room.**

| Sampling room | $\Sigma_7$tri-hepta | BDE-209 | BEH-TEBP | DBDPE | NBFRs |
|---|---|---|---|---|---|
| H1R1 | 0.277 | 0.508 | 0.323 | 0.81 | 0.55 |
| H1R2 | 0.269 | 0.232 | 0.012 | 0.054 | 0.006 |
| H1R3 | 0.359 | 0.576 | 0.411 | 0.613 | 0.285 |
| H2R1 | 0.575 | 0.247 | 0.219 | 0.438 | 0.335 |
| H2R2 | 0.0003 | 0.233 | 0.939 | 0.217 | 0.557 |
| H2R3 | 0.006 | 0.109 | 0.561 | 0.001 | > 0.001 |
| H3R1 | 0.71 | 0.341 | 0.102 | 0.055 | 0.024 |
| H3R2 | 0.052 | 0.347 | 0.66 | 0.405 | 0.572 |
| H3R3 | 0.071 | 0.244 | 0.994 | 0.785 | 0.992 |

**Appendix 3: *p* values obtained from the T-test comparison of concentrations of BFRs between the elevated surface dust and floor dust within the same room.**

| Sampling room | $\Sigma_7$tri-hepta | BDE-209 | BEH-TEBP | DBDPE | NBFRs |
|---|---|---|---|---|---|
| H1R1 | 0.022 | 0.045 | 0.138 | 0.026 | 0.062 |
| H1R2 | 0.031 | 0.042 | 0.071 | 0.573 | 0.3 |
| H1R3 | 0.046 | 0.058 | 0.029 | 0.398 | 0.003 |
| H2R1 | 0.007 | 0.089 | 0.096 | 0.108 | 0.11 |
| H2R2 | 0.056 | 0.107 | 0.68 | 0.012 | 0.199 |
| H2R3 | 0.041 | 0.013 | 0.048 | 0.002 | 0.205 |
| H3R1 | 0.15 | 0.354 | 0.047 | 0.016 | 0.056 |
| H3R2 | 0.201 | 0.03 | 0.04 | 0.393 | 0.037 |
| H3R3 | 0.042 | 0.092 | 0.008 | 0.34 | 0.003 |

**Appendix 4: *p* values obtained from the ANOVA comparison of concentrations of individual PBDEs and NBFRs in different particle size fractions.**

| Fraction | | *P* values | | | | | |
|---|---|---|---|---|---|---|---|
| | | **Σtri-hepta** | **BDE-209** | **BTBPE** | **EH-TBB** | **BEH-TEBP** | **DBDPE** |
| **BD (< 250 µm)** | P1 | 0.015 | 0.779 | 0.114 | 0.378 | 0.026 | 0.867 |
| | P2 | 0.966 | 0.243 | 0.101 | 0.313 | 0.161 | 0.082 |
| | P3 | 0.002 | 0.259 | 0.876 | 0.79 | 0.013 | 0.651 |
| **P1 (125-250 µm)** | BD | 0.015 | *0.779* | 0.114 | 0.378 | 0.026 | 0.867 |
| | P2 | 0.003 | 0.679 | 0.874 | 0.096 | 0.003 | 0.349 |
| | P3 | < 0.001 | 0.608 | 0.469 | 0.829 | 0.001 | 0.921 |
| **P2 (63-125 µm)** | BD | 0.966 | 0.243 | 0.101 | 0.313 | 0.161 | 0.082 |
| | P1 | 0.003 | 0.679 | 0.874 | 0.096 | 0.003 | 0.349 |
| | P3 | < 0.001 | 0.575 | 0.592 | 0.463 | 0.017 | 0.069 |
| **P3 (< 63 µm)** | BD | 0.002 | 0.259 | 0.876 | 0.79 | 0.013 | 0.651 |
| | P1 | < 0.001 | 0.608 | 0.469 | 0.829 | 0.001 | 0.921 |
| | P2 | < 0.001 | 0.575 | 0.592 | 0.463 | 0.017 | 0.069 |

**Appendix 5: ANOVA test results of comparison of carbon contents in different particle size fractions (BD= bulk dust, P1 = 125-250 µm, P2 = 63-125 µm and P3 = 25-63 µm)**

| TOC | | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval for Difference | |
|---|---|---|---|---|---|---|
| | | | | | Lower Bound | Upper Bound |
| P1 | P2 | -1.550 | .711 | .066 | -3.232 | .133 |
| | P3 | -.061 | 2.175 | .978 | -5.204 | 5.083 |
| | BD | .301 | 1.109 | .794 | -2.320 | 2.923 |
| P2 | P1 | 1.550 | .711 | .066 | -.133 | 3.232 |
| | P3 | 1.489 | 1.725 | .417 | -2.590 | 5.567 |
| | BD | 1.851* | .663 | .027 | .283 | 3.419 |
| P3 | P1 | .061 | 2.175 | .978 | -5.083 | 5.204 |
| | P2 | -1.489 | 1.725 | .417 | -5.567 | 2.590 |
| | BD | .362 | 1.191 | .770 | -2.453 | 3.177 |

**Appendix 6: Pearson Correlation results describing the relationship between BFR concentrations in dust samples collected by a researcher (RCDL and RCDB) and household vacuum (HHVD) approaches**

| HHVD | RCDL | | RCDB | |
|---|---|---|---|---|
| | **Pearson Correlation** | ***P* value** | **Pearson Correlation** | ***P* value** |
| BDE-47 | 0.273 | 0.391 | 0.225 | 0.481 |
| BDE-99 | 0.611 | 0.035 | 0.549 | 0.064 |
| BDE-153 | 0.369 | 0.202 | 0.396 | 0.202 |
| tri-hexa | 0.583 | 0.047 | 0.588 | 0.044 |
| BDE-183 | 0.410 | 0.186 | 0.422 | 0.172 |
| BDE-209 | 0.532 | 0.075 | 0.350 | 0.265 |
| EH-TBB | 0.423 | 0.171 | 0.557 | 0.060 |
| BTBPE | 0.270 | 0.395 | 0.334 | 0.288 |
| BEH-TEBP | 0.793 | 0.002 | 0.883 | <0.001 |
| DBDPE | 0.643 | 0.024 | 0.634 | 0.027 |

**Appendix 7: BFR exposure assessment comparison between RCD (researcher –collected dust) and HHVD (household vacuum dust)**